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Epoxidation of olefins catalyzed by novel Mn(III) and Mo(IV) Salen complexes immobilized on mesoporous silica gel Part I. Synthesis and characterization of homogeneous and immobilized Mn(III) and Mo(IV) Salen complexes

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Abstract

New ways of the covalent immobilization of Mn(III) and Mo(IV) Salen complexes on a mesoporous silica support to produce a stable heterogeneous catalyst for epoxidation reactions are reported. Peptide and ester interactions were employed to anchor the metal Salen complex on the organo-modified silica framework. Electrospray MS, FTIR, TGA, ICP-OES and elemental analysis were used for quantitative and qualitative analyses of the immobilized Salen complexes. The results confirm the location of the metal Salen complex inside the mesopores covalently attached to the silica framework.

Keywords: Immobilized Mn- and Mo-Salen; Peptide and ester immobilizations; Electrospray MS; FTIR; Thermogravimetry

1. Introduction

During the last decade a number of powerful asymmetric reactions have emerged as a result of the growing need to develop efficient and practical syntheses of biologically active compounds, production of fine chemicals and polymers. Various epoxides are among the most widely used intermediates in organic synthesis as well as pharmaceuticals, acting as precursors to complex molecules [1]. As a result, there are varieties of investigation routes for the development of different catalysts for epoxidation reactions such as heterogeneous supported metal oxides [2,3] as well as homogeneous transition metal complexes [4].

Mn(III) complexes of the Schiff base with a ON–NO coordination sphere, which are known as Salen complexes (Salen—*N*,*N*′-bis(salicylidene)-ethylendiamine), have been reported by Jacobsen at al. [5], Katsuki and co-workers [6] and Kochi and co-workers [7] as one of the most efficient homogeneous catalysts in asymmetric catalytic reactions. Their applications have grown rapidly and a broad range of asymmetric catalytic reactions has been described including oxidations, additions and reductions such as epoxidation of olefins, epoxide ring opening, Diels–Adler reaction, imine cyanation, conjugate addition, carbon dioxide insertion into epoxides, etc. [4,8–11].

Homogenous catalysis often provides better results in achieving high activity and enantioselectivity in comparison to heterogeneous catalysis. Many effective heterogeneous catalysts (TS-1, Al-MCM-41, etc.) show high selectivity and catalytic activity, but they do not provide the required enantioselectivity to the desired products. The preparation of new heterogeneous catalysts by immobilizing catalytically active metal Salen complexes on an insoluble polymer support [12], porous materials such as zeolites, MCM-41 and analogous materials [13–16] or intercalation in clays [17,18] has received a lot of attention. The potential benefits from heterogenization include facilitation of catalyst separation from reagents and reaction products as well as simplification for catalyst recycle. There is a wide variety of different ways of immobilization described in the literature. However, among them the anchoring of Salen complexes by coordination demonstrated disappointing results due to significant leaching in a single catalytic run [19].

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In this study, we report the syntheses of new active and stable immobilized Salen catalysts and their application in the epoxidation of olefins. In the first part we present two novel methods for the covalent attachment of manganese and molybdenum Salen complexes to organo-modified silica supports and its investigation by spectroscopic methods. In the second part catalytic results will be reported.

2. Experimental

2.1. Chemicals

The solvents used in the syntheses were purchased as extra dry from Acros Organics and used without further purification. Commercially available starting materials were used as received, unless stated. 3,5-Di-*tert*-butylsalicylaldehyde [20] and bis(tetrahydrofuran) manganese (II) chloride ($MnCl_2(THF)_2$) [21] were prepared as described in literature. The amorphous mesoporous silica gel Köstrosorb 1015 used for immobilization was purchased from Chemiewerk Bad Köstritz GmbH, Germany (BET surface area is 350 $m^2\,g^{-1}$, pore volume is 1.1 $cm^3\,g^{-1}$, the average pore diameter is 12.5 nm).

2.2. Characterizations

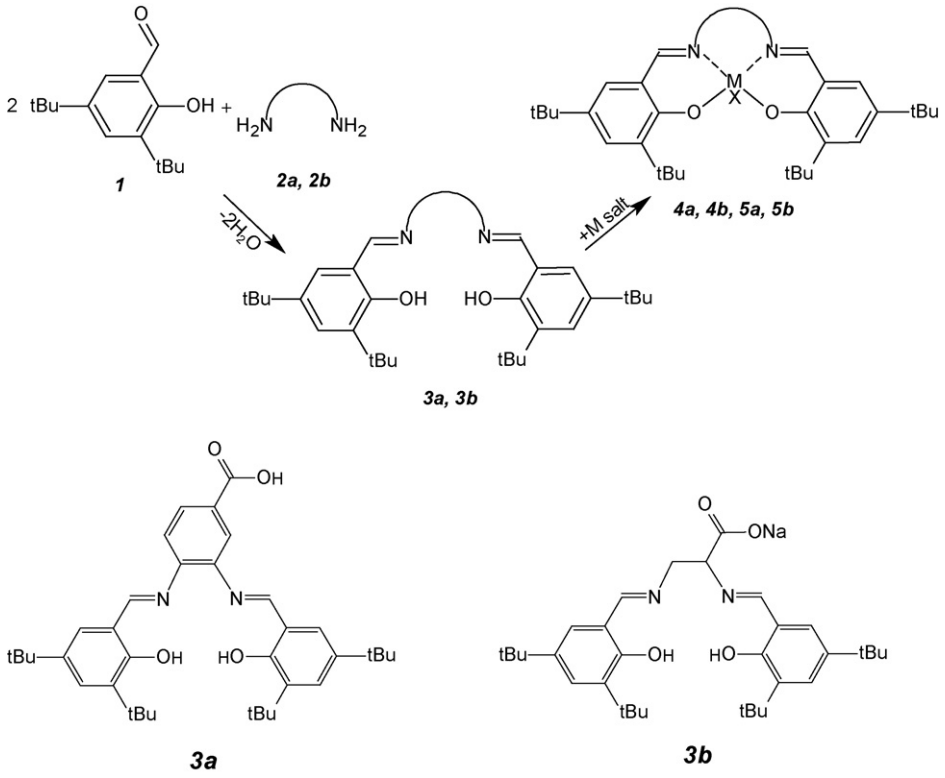
Elemental analysis. Elemental analyses were performed on a Heraeus CHN Rapid Analyzer. The catalyst loading in the immobilized catalyst was defined by elemental analysis of metal using inductively coupled plasma-optical emission spectrometry (ICP-OES) in Wolfener Analytik GmbH of Bitterfeld, Germany.

TGA. Thermogravimetric analyses were carried out using a STA 409 equipment (Netzsch) coupling with a MS detector (Balzer Quadrupole). About 20 mg of the sample was heated at a heating rate of 10 K min^{-1} from ambient temperature up to 900 °C under dry helium flow with corundum as a standard. The samples were pretreated in vacuum (10^{-1} mbar) at 50 °C.

FTIR. Infrared spectra were recorded using a Bruker IFS 66 spectrometer equipped with a heated and evacuated IR cell with CaF_2 windows, connected to a gas dosing-evacuation system. FTIR spectra of unsupported Salen complexes were recorded in KBr pellets at room temperature from 4000 to 400 cm^{-1}. For the characterization of the modified silica gel as well as the immobilized Salen complexes the sample powder was pressed into self-supporting discs with a diameter of 20 mm and a weight of 60 mg and activated by evacuation at room temperature.

ESI MS. Electrospray ionization technique is the method to study large molecular size complexes. The method transfers pre-existing ions from solution to the gas phase, and is ideal for inorganic and organometallic compounds that do not form gas-phase ions by conventional ionization methods like electron impact mass spectrometry. Additionally, ESI has proven to be a soft ionization method that keeps intact even weakly bound ligands in complex ion.

The unsupported metal Salen complexes as well as immobilized complexes were analyzed by electrospray ionization mass spectrometry. The samples were introduced by injection of the solution with 2 μl min^{-1} by a syringe pump. All the mass spec-



Scheme 1. The general procedure of Salen complex synthesis (**2a**: 3,4-diaminobenzoic acid; **2b**: (*R*,*S*)-2,3-diaminopropionic acid monohydrochloride; **3a**, **3b**: Schiff base structures used for syntheses of the corresponding metal Salen complexes; **4a**, **4b**: MX = Mn(III)–Cl; **5a**, **5b**: MX = Mo(IV)═O).

tra were recorded using FT-ICR mass spectrometer APEX II from Bruker. The data were acquired using Xmass software. The ESI capillary voltage was maintained at 4.5 kV, and nitrogen was used as desolvation and nebulization gas. The dry gas temperature was kept at 200 °C.

2.3. Synthesis of Mn(III) Salen complexes

The general route for the synthesis of metal Salen complexes is shown in Scheme 1. Schiff bases are easily prepared by the condensation of salicylaldehyde and diamine, followed by metallation to obtain the desired metal Salen complex [22].

*Schiff base **3a***. The Schiff base was prepared as follows: diamine **2a** (10.0 mmol) was suspended in 50 ml of tetrahydrofuran (THF). Then salicaldehyde **1** (20.0 mmol) dissolved in 40 ml THF and 0.5 M $ZnCl_2$ (10.0 mmol) solution in THF were added dropwise to the suspension. The resulting mixture was refluxed for 45 min followed by the solvent removal under reduced pressure. The residue was then dissolved in 25 ml of methanol; the insoluble residue was filtered and washed with methanol. The product was finally recovered as a yellow–green solid (93% yield).

*Mn(III) Salen complex **4a***. The corresponding Schiff base **3a** (1.2 mmol) was completely dissolved in 70 ml THF followed by addition of $MnCl_2(THF)_2$ (1.2 mmol) by portions within 15 min. The yellow–brown suspension was vigorously stirred at room temperature for 1 h and then refluxed for 0.5 h. The mixture was cooled down to room temperature and triethylamine (TEA) (2.4 mmol) was slowly added. Air was bubbled through the dark brown solution for 45 min; afterwards the solvent was evaporated. The residue was dissolved in 20 ml of toluene and stirred at room temperature for 2 h. The mixture was filtered and washed with toluene. The resulting black foam-solid of Mn(III) Salen complex **4a** (89% yield) was collected as raw product from the filtrate under reduced pressure.

*Schiff base **3b***. The Schiff base **3b** (Scheme 1) was prepared as follows: diamine **2b** (7.1 mmol) was suspended in 25 ml of methanol followed by addition of a sodium hydroxide solution in 5 ml of methanol (14.2 mmol). Salicylic aldehyde **1** (14.2 mmol) was dissolved in 50 ml of methanol and dropwise added to the stirred solution during 25 min. The yellow reaction mixture was heated under reflux for 20 min. Finally, insoluble impurities were collected by filtration and the solvent was evaporated under vacuum to get the Schiff base **3b** as a yellow precipitate (89% yield).

*Mn(III) Salen complex **4b***. Schiff base **3b** (1.6 mmol) was dissolved in 50 ml THF followed by addition of triethylamine (3.2 mmol). Subsequently $MnCl_2(THF)_2$ (1.6 mmol) was added by portions to the mixture within 15 min. The dark brown mixture was refluxed for 1.5 h, afterwards air was blown through the solution for 40 min. Then it was refluxed anew for 2 h followed by evaporation of the solvent. In order to remove the formed triethylammonium chloride the dark solid residue was dissolved in 25 ml of toluene and separated by filtration. The dark brown solid was recovered from the filtrate by rotary evaporation and dried in vacuum (72% yield).

2.4. Synthesis of Mo(IV) Salen complexes

The synthesis of the Mo-Salen complexes was carried out in two stages (Scheme 1). Both of Mo(IV) Salen complexes **5a** and **5b** were prepared with the same procedure [23] as follows: $Mo(CO)_6$ (2 mmol) was dissolved in 100 ml of dry THF followed by addition of the above described Schiff bases **3a** or **3b** (2 mmol). The light brown solution was heated under reflux for 24 h. The mixture was filtered followed by solvent evaporation. The product was recovered as a black foam-solid (95% yield).

The Salen complexes **4** and **5** were used in the following synthesis stages without further purification.

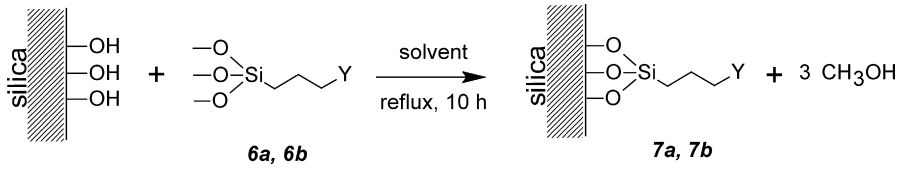
2.5. Preparation of the organo-functionalized silica structures *7a* and *7b*

(3-Aminopropyl)trimethoxysilane **6a** and (3-iodopropyl) trimethoxysilane **6b** were anchored onto the silica surface via a post-synthesis grafting method to prepare organo-modified mesoporous materials (Scheme 2). The procedure of synthesis was similar to that described by Yokoi et al. with some modifications [24]. The amorphous silica gel was preliminary heated in a vacuum oven at 70 °C for 3 h to remove adsorbed water. A 5.0 g of the so-pretreated silica powder were suspended in 90 ml of dry toluene followed by addition of **6a** (28 mmol). The mixture was vigorously stirred under reflux for 10 h. The resulting suspension was filtered through a Buchner funnel supplied with a fine-porous filter paper. The collected powder **7a** was washed overnight in a Soxhlet extractor using 2-propanol as a solvent and dried in air at 100 °C for 5 h.

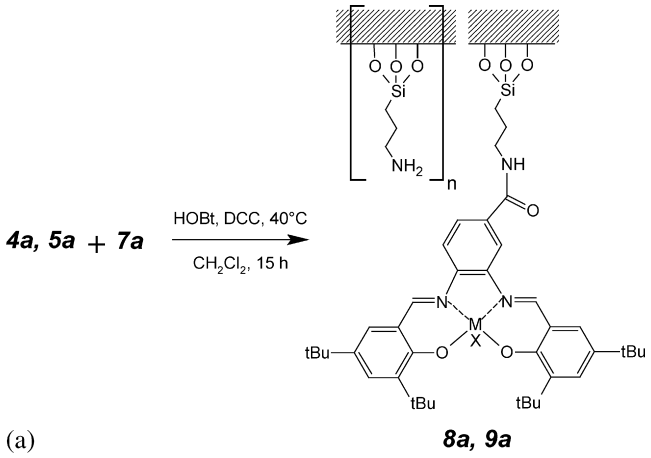
In case of the iodo-functionalized silica **7b** the procedure was similar to that above described, but the amount of **6b** used was lower in comparison to **6a**; 2.0 ml (10 mmol) of **6b** were used and the reaction was running at room temperature.

2.6. Immobilization of the Salen complexes

Peptide and ester covalent bonding interactions were utilized and explored to synthesize heterogeneous catalysts by immobilization of the metal Salen complexes on the modified surfaces of silica gel (Scheme 3).



Scheme 2. The modification of the silica surface by organo-silanes (**6a**, **7a**: Y = NH_2; **6b**, **7b**: Y = I).



Scheme 3. The ways of Salen complexes immobilization (**8a**, **8b**: MX = Mn(III)–Cl; **9a**, **9b**: MX = Mo(IV)=O). (a) Peptide bonding, $n = 6$–9. (b) Ester bonding, $n = 20$–120.

2.7. The peptide bound immobilization (*8a*, *9a*)

Both of the complexes **4a** and **5a** have a carboxylic functional group in their structures (Scheme 1, **3a**). The carboxylic groups were used to obtain the peptide interaction with amino-groups from modified silica **7a** and, consequently, to built a stable covalent bond between silica framework and complex.

The synthesis of peptide bound immobilization was performed using the peptide coupling procedure [25] as shown in Scheme 3a. Salen complex as **4a** or **5a** (1.8 mmol) were dissolved in 30 ml of methylene chloride, afterwards 1.0 mmol of 1-hydroxy-1H-benzotriazole (HOBt) was added in portions. After 10 min of vigorous stirring 5.0 mmol of *N*,*N*′-dicyclohexylcarbodiimide (DCC) solution in 3 ml CH_2Cl_2 was also added. The mixture was stirred at room temperature for 40 min until 1.3 g (1.87 mmol of amino-groups) of silica **7a** pretreated in vacuum at 75 °C were slowly added to the mixture. The resulting suspension was stirred under reflux for 15 h followed by Soxhlet extraction with ethanol for 30 h and acetone for 10 h. The final products **8a** or **9a** were dried in air.

2.8. The ester bound immobilization (*8b*, *9b*)

To obtain ester interaction with the iodine of the modified silica structure (**7b**) Salen complexes containing the sodium salt of carboxylic acid (**4b**, **5b**) as functional groups were selected.

The ester bound immobilization procedure is illustrated in Scheme 3b and was carried out as follows: the metal Salen complex **4b** or **5b** (1.5 mmol) was dissolved in 8 ml of dimethyl formamide (DMF) and 1.0 g of iodo-functionalized silica gel (1.26 mmol of iodopropyl groups) was slowly added as a solid. The dark brown suspension was vigorously stirred at 75 °C for 28 h. The product of immobilization was filtered and washed on the Soxhlet extractor with methanol for 40 h. The final products **8b** and **9b** were dried in air.

3. Results and discussion

In order to immobilize a metal Salen complex covalently, functional parts appropriate for the covalent interaction must be present. Mostly functional groups of the aromatic rings corresponding to salicylic aldehyde of the individual Salen molecules were previously used for this purpose [13,15]. However, the efficiency and activity of the immobilized catalyst can decrease due to the absence of a local C_2 symmetry in the Salen unit [26]. Moreover, the condensation of two different salicylaldehyde derivatives with the diamine provides a statistical mixture of the unsymmetrical and symmetrical Schiff bases that are only readily separated by preparative HPLC or flash chromatography. Therefore, the use of diamine derivatives containing active groups for covalent interaction without changing the symmetry of the Schiff bases seems to be the crucial point.

The elemental and the NMR analyses of the Schiff bases (**3a** and **3b**) and metal Salen complexes (**4a**, **4b**, **5a** and **5b**) showed a purity of about 92–95% for all synthesized compounds and correlated well with literature results [22].

3.1. Elemental analysis and ICP-OES

The total content of the reactive groups (aminopropyl and iodopropyl) in **7a** and **7b** was determined by CHN and CH elemental analyses, respectively. The amount of iodine was calculated in terms of CH elemental analysis data corresponding to the propyl groups of **7b**. The amounts of aminopropyl and iodopropyl substituents coupled to the silica supports were 1.44 and 1.26 mmol g^{-1}, respectively (Table 1).

ICP-OES analysis allows to determine the manganese and molybdenum content in immobilized Mn and Mo-Salen complexes **8a**, **8b**, **9a** and **9b**. In case of peptide immobilizations (**8a**, **9a**) the results demonstrate Mn and Mo amounts to be 1.2 and 1.5 wt.%, respectively. Thus, the concentration of metal Salen complex with respect to silica (SiO_2) is 0.22 for **8a** and 0.16 mmol g^{-1} for **9a**. For the ester immobilization the results of ICP-OES are the following: 0.41 and 0.1 wt.% (0.07 and 0.01 mmol g^{-1}) of manganese and molybdenum, respectively.

The results demonstrate that the percentage of peptide interaction of the Salen complex with amino-functionalized silica is ca. 14%, hence, the content of free aminopropyl groups after

Table 1
Elemental and OES analysis of the modified silica structures **7a**, **7b** and the immobilized complexes **8a**, **8b**, **9a**, **9b**

Compound	ICP-OES, metal loading (mmol g^{-1})	Elemental analysis (wt.%)				Fragment loading[a] (mmol g^{-1})
		C	H	N	Cl	
7a	–	5.91	1.88	1.73	–	1.44
7b	–	4.55	1.63	–	–	1.26
8a	0.22	16.00	2.04	2.13	1.01	0.27
8b	0.07	6.90	1.81	0.22	0.26	0.07
9a	0.16	14.21	2.81	2.50	–	0.18
9b	0.01	4.98	1.74	–	–	0.01

[a] Organic content inside the silica structure, calculated with respect to elemental analysis.

immobilization with respect to anchored molecules of Salen complex (*n*) is about 6–9 (Scheme 3a). The corresponding results for ester immobilized complexes show considerably lower loading of Salen complexes inside the porous silica structure in comparison to the peptide immobilized catalysts: the percentage of ester bonding is ca 6% for the Mn-Salen complex and ca. 1% for the Mo-Salen complex. Consequently, the number of free iodopropyl groups corresponding to one Mn or Mo-Salen molecule is about 20 or 120, respectively.

The influence of residual free amino and iodopropy groups on the surface support was additionally investigated. Such tests show that the presence of these functionalized groups did not cause a possible non-productive decomposition of peroxide as well as a likely epoxide ring opening reaction of the resulting epoxide in catalytic epoxidation. Moreover, to exclude any probability of the functionalized surface groups influence the catalytic epoxidation experiment with homogeneous Salen complexes mixed with organo-functionalized silica in corresponding amount were performed and showed that there was no difference in epoxidation results for such mixtures in comparison to the pure homogeneous catalyst. These results will be discussed in detail in second part of publication.

The significant differences between peptide and ester bound loading can be explained by various reactivities inside the porous system for the different ways of bonding. Besides, the obtained peptide bond possesses higher stability in comparison to the ester bond.

3.2. TGA

The organic content in the modified silica **7a** and **7b** was also determined by TGA assuming that the weight loss occurring at ca 500 °C in case of **7a** and at ca. 350 °C for **7b** can be attributed to the thermal decomposition of the aminopropyl and iodopropyl groups, respectively.

The results of the thermogravimetry analyses are presented for the molybdenum immobilized Salen complexes, for the manganese complexes similar results were obtained. The differential thermogravimetry (DTG) values for **9a** and **9b** versus the temperature are given in Fig. 1. The small weight loss at about 100 °C in both systems is corresponding to the desorption of water from the silica. The weight loss in the temperature range of 200–400 °C must be referred to the first thermal decomposition steps of the Salen complexes. The main weight loss in the temperature range of 400–550 °C corresponds to the splitting of the Salen molecules coupled to the silica support since the weight of the Salen complex is much higher than the organic content of the functionalized groups of the surface modification, namely aminopropyl and iodopropyl (Table 1). The final peaks in the region of 700–800 °C in both cases indicate a weight loss (2–7%) due to partly thermal decomposition of the silica structures. Thus, the weight loss of ca 11 wt.% at 430 °C for the peptide immobilization of Mo-Salen complex and ca. 3.6 wt.% at 534 °C for the ester immobilized complex indicate the difference in loading of the Salen complexes for the different types of bonding (Fig. 1). Moreover, TG allows to observe the difference in thermal stability of the covalent interaction when comparing peptide and ester bonding. Hence, the ester immobilized system **9b** exhibits higher stability of the covalent bond in contrast to the reactivity in obtaining this bond.

3.3. FTIR spectroscopic analysis

To interpret the FTIR spectra of immobilized Salen complexes the results are shown as comparison between the adducts, i.e. **7** and **4**, and the resulting product **8** (cf. Figs. 2 and 3 for 1330–2000 cm^{-1}).

The FTIR spectra of the organo-modified silica samples **7a** and **7b** show characteristic vibration bands at around 1101, 802

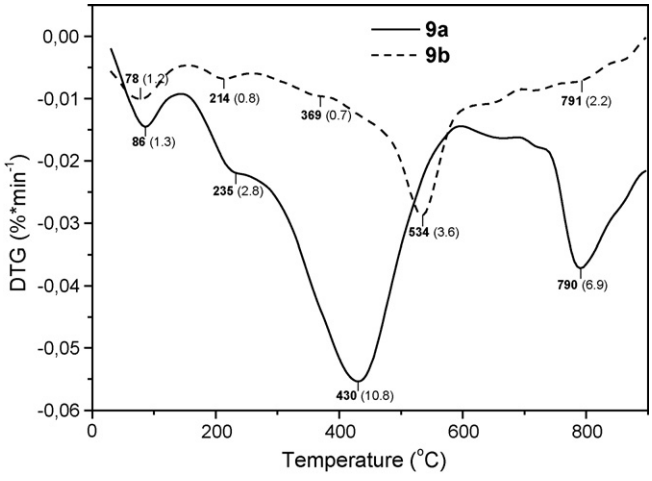


Fig. 1. DTA spectra of peptide (**9a**) and ester (**9b**) bound immobilized Mo(IV) Salen complex. The values correspond to the average temperature with weight loss percentage given in parentheses.

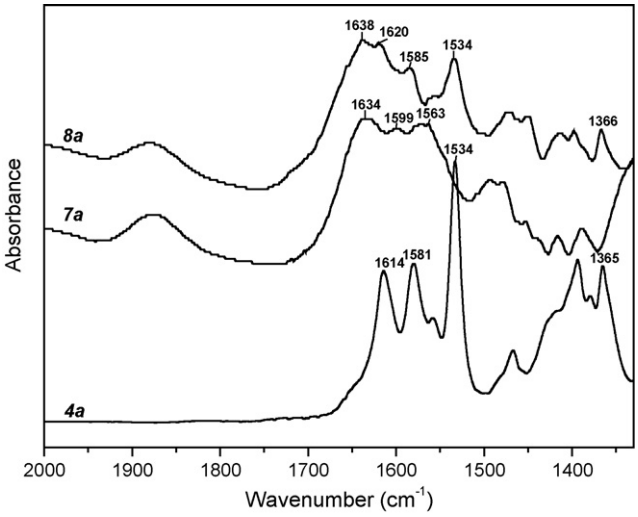


Fig. 2. FTIR spectra of Mn(III) Salen complex **4a**, amino-functionalized silica **7a** and peptide bound immobilized Mn-Salen complex **8a**.

and 470 cm^{-1}, corresponding to the stretching, bending and out of plane deformation vibrations of Si–O–Si bonds, respectively [27,28]. The broad peak with a maximum at 1101 cm^{-1} and a broad shoulder at 1200 cm^{-1} can be attributed to a of Si–C vibration. The small peaks observed in the spectral range of 1350–1500 cm^{-1} might be attributed to the C–H asymmetric and symmetric stretching vibrations, the deformation of NH_2 (in case of **7a**), and the CH_2 and CH_3 groups of the aminopropyl (**7a**) and iodopropyl (**7b**) parts [13]. A very broad absorption band centered at 3450 cm^{-1} is assigned to hydrogen bound surface Si–OH groups as well as NH_2 for amino-functionalized silica **7a**.

FTIR spectra of the unsupported and the immobilized metal Salen complexes (for both cases **a** and **b**) are comparable for manganese and molybdenum. The IR spectra of the manganese systems are presented in Figs. 2 and 3. Functional groups could be identified for the peptide bound immobilized complex **8a** (Fig. 2). The Mn(III) Salen complex **4a** exhibits strong bands at 1534, 1581 and 1614 cm^{-1} due to conjugated aromatic bonds ν(C=C), ν(C=N) and ν(C=O) of carboxylic group, respectively. The bands appearing at 1585 and 1620 cm^{-1} for the immobilized complex **8a** are shifted ν(C=N) and ν(C=O) vibrations of the unsupported Salen complex **4a**. The peak at 1365 cm^{-1} for **4a** can be assigned to ν(C–O) [29] and it appears in the immobilized Salen complex at the same wavenumber (Fig. 2).

The IR spectra for the ester bound immobilized Mn complex **8b** and its precursors are illustrated in Fig. 3. The intensive broad band at 1652 cm^{-1} for the immobilized complex must be the merged peak of the bands at 1616 cm^{-1} corresponding to the ν(C=O) vibration of the Mn-Salen complex **4b** and at 1634 cm^{-1} that contains C–H stretching vibrations of the silica support **7b** with blue shift. By analogy with the peptide bound immobilized system the unsupported complex **4b** exhibits a ν(C–O) bond at 1366 cm^{-1}, which appears in the spectrum of **8b** as a small peak at 1358 cm^{-1}. In case of the ester immobilized complex the spectra cannot be easily interpreted because of the low loading of the Salen complex (ca. 6%).

3.4. ESI MS

3.4.1. ESI MS analysis of Mn-Salen complexes (*4a, 4b*)

Both unsupported Mn-Salen complexes **4a**, **4b** were analyzed by ESI MS in different solvent mixtures as well as in the presence of sodium salts in order to clearly distinguish the molecular peaks of the Salen complexes (Table 2).

The positive ion ESI mass spectrum of the complex **4a** (molecular mass is 672.3; atom content is $C_{37}H_{46}N_2O_4MnCl$ = [**4a**]) in the chloroform ($CHCl_3$)/acetonitrile (ACN) solvent system containing sodium formate (HCOONa) shows major ions corresponding to $[\mathbf{4a} - HCl + H^+]^+$, $[\mathbf{4a} - HCl + Na^+]^+$ and $[2^*\mathbf{4a} - HCl + H^+]^+$ fragments (Fig. 4). The loss of HCl is typical fragmentation for this class of substances. In case of the solvent systems $CHCl_3$/ACN and THF/ACN the resulting spectra demonstrate intensive peaks that are corresponding to the appropriate Schiff base fragment

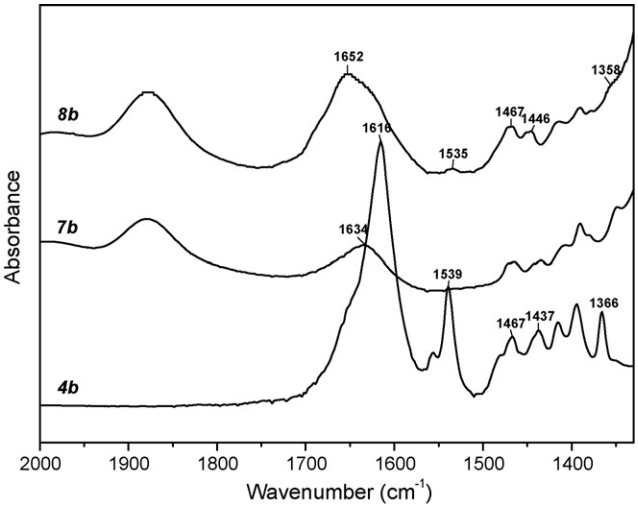


Fig. 3. FTIR spectra of Mn(III) Salen complex **4b**, iodo-functionalized silica **7b** and ester bound immobilized Mn-Salen complex **8b**.

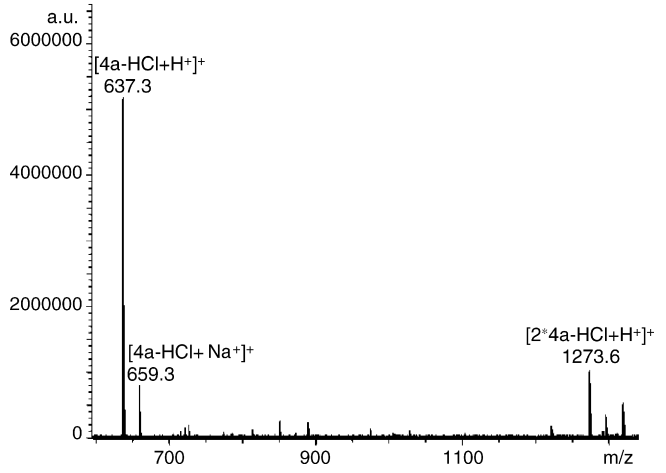


Fig. 4. ESI MS spectra of Mn(III) Salen complex **4a** in chloroform–acetonitrile solvent system containing sodium formate.

Table 2
ESI MS fragments of Mn-Salen complexes at different solvent conditions

Conditions	Mn-Salen			
	4a		**4b**	
	MS fragment	*m/z*	MS fragment	*m/z*
	[**3a** + H^+]$^+$	585.4		
$CHCl_3$/ACN	[**4a** − Cl^-]$^+$	637.3	[**4b** − NaCl + TEA + H^+]$^+$	690.4
	[**4a** + TEA + H^+]$^+$	774.3		
	[**4a** − HCl + H^+]$^+$	637.3	[**4b** − NaCl + H^+]$^+$	589.3
$CHCl_3$/ACN + Na	[**4a** − HCl + Na^+]$^+$	659.3	[**4b** − NaCl + Na^+]$^+$	611.3
	[2*__4a__ − HCl + H^+]$^+$	1273.6	[**4b** − NaCl + TEA + H^+]$^+$	690.4
	[**3a** + H^+]$^+$	585.4	[**4b** − NaCl + H^+]$^+$	589.3
THF/ACN	[**4a** − Cl^-]$^+$	637.3	[**4b** − NaCl + Na^+]$^+$	611.3
	[**4a** + TEA + H^+]$^+$	774.3	[**4b** − NaCl + TEA + H^+]$^+$	690.4
	–	–	[**4b** − NaCl + H^+]$^+$	589.3
MeOH	–	–	[**4b** − NaCl + Na^+]$^+$	611.3
	–	–	[**4b** − NaCl + TEA + H^+]$^+$	690.4

[**3a** + H^+]$^+$ (molecular mass of the Schiff base **3a** ($C_{37}H_{48}N_2O_4$) is 584.4), [**4a** − Cl^-]$^+$ and [**4a** + TEA + H^+]$^+$.

The Mn-Salen complex **4b** with molecular mass 646.2 ($C_{33}H_{45}N_2O_4MnClNa$ = [**4b**]) was analyzed by ESI mass spectroscopy at the same conditions in the presence of HCOONa and without it. In case of sodium salt free conditions the positive ions in $CHCl_3$/ACN solvent system appear at *m/z* 690.4 that corresponding to [**4b** − NaCl + TEA + H^+]$^+$. In methanol as a solvent or in the THF/ACN solvent system as well as in the sodium formate containing $CHCl_3$/ACN mixture three characteristic fragments of Mn-Salen **4b**: [**4b** − NaCl + H^+]$^+$, [**4b** − NaCl + Na^+]$^+$ and [**4b** − NaCl + TEA + H^+]$^+$ were observed. This shows that the ESI MS technique allows to observe major fragments typical for the both Mn-Salen complexes.

The presence of triethyl amine (TEA) in the fragments of **4a** and **4b** must be from its residue after synthesis of complex (see Section 2.3). Granting that the samples were preliminary treated in vacuum at 50 °C the results show that such pretreatment does not allow to evacuate coordinately connected with Salen complex TEA.

3.5. ESI MS analysis of immobilized Mn-Salen complexes (8a, 8b)

The ESI MS experiments of the immobilized complexes **8a** and **8b** carried out in neutral condition with different solvent systems ($CHCl_3$/ACN) proved the absence of Salen fragments that consequently shows the presence of only coupled Salen complex molecules inside the silica structure. The immobilized complexes were also identified using ESI with a previous treatment of the sample by formic acid or by trimethylamine (TMA) to test the stability of the immobilized systems by basic or acidic media.

Immobilized manganese complexes at the neutral conditions in $CHCl_3$/ACN solvent mixture did not show characteristic MS signals for Salen complexes. The ESI mass spectra of peptide bound Mn-Salen complex **8a** after treatment by TMA in $CHCl_3$/ACN solvent system showed a positive peak at *m/z* 568.4 which can be assigned to the fragment of the Mn-Salen complex without the central aromatic ring. In case of pretreatment with formic acid the characteristic peak of the unsupported Salen complex appears at *m/z* 637.3.

The results prove that basic or acidic environment initiated chemical decomposition of the immobilized system due to breaking the bond between complex and solid.

The ESI MS analysis of the ester bound immobilized Mn-Salen **8b** complex showed similar effects.

4. Conclusion

Manganese and molybdenum Salen complexes were successfully immobilized on a mesoporous silica support. The structure of the resulting heterogeneous system was confirmed by elemental analysis as well as spectroscopic analyses such as FTIR, ESI MS and ICP-OES. The presence of metal and its content in immobilized complexes were determined by ICP-OES. The results showed the loading of metal Salen complexes on modified silica surfaces for the chosen immobilization conditions to be at a percentage of ca. 14% and 1–6% for peptide and ester bound interactions, respectively. It must be noted that although the immobilization processes were not fully optimized for a possible higher loading of the resulting heterogeneous structures are newly synthesized immobilized catalysts which could be explored in at least three consecutive catalytic epoxidation runs without evident lost of activity. The resulting catalysts left options for a further improvement during immobilization. The FTIR spectra demonstrate the presence of metal Salen units inside the organo-modified silica surface. ESI mass spectrometry showed the spectra for both unsupported Salen complexes and proved structure and stability of the immobilized systems at different conditions. At neutral solvent system conditions no Salen complex MS spectra were observed indicating only coupled molecules of Salen complex excluding non-bound ones in the porous material. The catalytic epoxidation of some

olefins (cyclooctene, cyclohexane) in presence of different solvents such as chlorobenzene, toluene, tetrachloroethane, etc. and oxidants (*tert*-butylhydroperoxide, cumene hydroperoxide) has shown that the immobilized complexes are stable during repeated catalytic runs.

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