

Olefin epoxidation with H₂O₂ in the presence of Mn(II) dicarboxylate coordination polymer catalysts

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Abstract The Mn(II) dicarboxylate coordination polymers [Mn(μ -terephthalate)(H₂O)₂]_n, [Mn(μ -oxalate)(H₂O)₂]_n, and [Mn(μ -D-(–)-tartrate)]_n were prepared in water and characterized by FT-IR spectroscopy and CHN analysis. Particles of the terephthalate catalyst were also synthesized, by reaction of terephthalic acid and MnCl₂·4H₂O by a sonochemical method. The catalytic potential of these coordination polymers as slow-release sources of catalytically active Mn species was tested in the oxidation of cyclooctene to its epoxide in acetonitrile, using hydrogen peroxide as oxygen source. For the terephthalate species the catalytic activity was found to increase with increasing dielectric constant and dipole moment of the solvent (being highest in acetonitrile), with reaction temperature to a maximum at 60 °C, and with an imidazole co-catalyst (highest activity found for a imidazole-to-catalyst molar ratio of 20:1). Good activity with more than 64% conversion in 24 h was obtained for epoxidation of cyclooctene and cyclohexene, whereas low yields only were obtained from aryl-substituted olefins. Some *exo* versus *endo* regioselectivity was found for norbornene.

Keywords Olefin oxidation · Hydrogen peroxide · Coordination polymer · Manganese

Introduction

The catalytic epoxidation of olefins has been a subject of growing interest in the production of chemicals and fine chemicals. Because epoxides are key starting materials for a wide variety of products [1], much effort has been made to develop new active and selective epoxidation catalysts for processes that require elimination of by-products. Over the past decade, many systems using manganese porphyrin [2] or Schiff base [3–6] complexes as catalysts with various oxidants have been shown to oxidize unsaturated organic molecules effectively. More recently, a major focus of manganese-catalyzed oxidations has been to design catalysts which use hydrogen peroxide as the oxygen atom donor, because this oxidant is readily available, inexpensive, and produces water as its only by-product. Metal-catalyzed epoxidations of alkenes with hydrogen peroxide have been reviewed [7]. Burgess has used manganese(II) salts for epoxidation of olefins with H₂O₂ in the presence of NaHCO₃ [8]. TACN (1,4,7-triazacyclononane) complexes of manganese [9–12] have been used for olefin epoxidation with H₂O₂ and are very active, but the ligands are difficult to prepare. Interest in TACN-derived catalysts for alkene epoxidation with H₂O₂ originates largely from work at Unilever on potential detergent additives which oxidize, and thereby remove, organic stains [12].

Coordination polymers have been widely studied in synthetic chemistry and materials science. The synthesis of coordination polymers with different metal ions and ligands [13] has led to a wide range of potential application-oriented properties, including catalysis [14]. Coordination polymers

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with moderate stability and high lability are efficient catalysts in a vast range of chemical and biochemical processes [15–20] (specific examples are discussed in Refs. [21–25]). Manganese coordination polymers have been studied as oxidation catalysts [22, 26] and for their catalytic activity in H_2O_2 disproportionation [27].

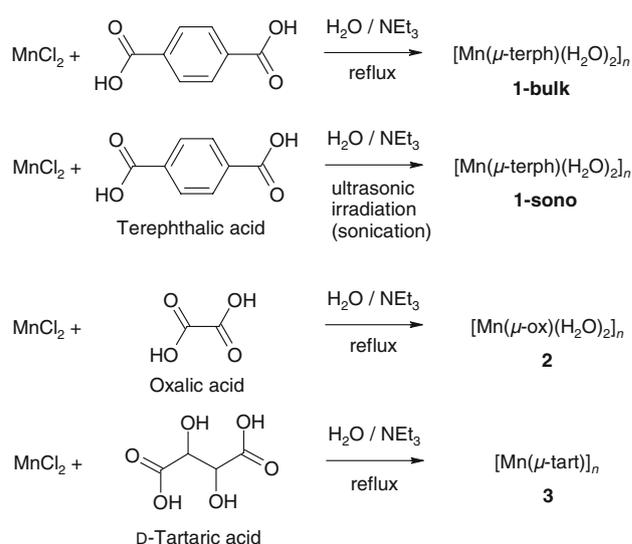
Multi-carboxylate ligands with suitable spacers, especially benzene-multicarboxylate ligands, are frequent choices for metal–organic networks [28–33].

This article focuses on the simple synthetic preparation of three Mn(II) dicarboxylate coordination polymers, including the preparation of $[\text{Mn}(\mu\text{-terph})(\text{H}_2\text{O})_2]_n$ (**1**) (terph = terephthalate, $^-\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2^-$) by a sonochemical method, and comparison of its catalytic activity.

Results and discussion

Characterization of the compounds

In this study, three different carboxylate compounds of manganese were synthesized. Reaction of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ with terephthalic acid and Et_3N in H_2O gave the white product $[\text{Mn}(\mu\text{-terph})(\text{H}_2\text{O})_2]_n$ as **1-bulk** in good yield. The Mn(II) material **1-sono** was obtained by reaction between triethylammonium terephthalate and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ with ultrasonication of the aqueous solution (Scheme 1). The infrared spectra of **1-bulk** and **1-sono** are identical and show ν_a and ν_s bands of carboxylate at 1,546 and 1,392 cm^{-1} , respectively (Fig. 1). Carboxylate groups which are chelating or coordinating with each O atom to a metal atom exhibit differences between the asymmetric and symmetric stretching frequencies, which are less than the ionic value ($\Delta\bar{\nu} = 164 \text{ cm}^{-1}$ for the acetate ion) [34]. For compound **1** $\Delta\bar{\nu} = 1,546 - 1,392 = 154 \text{ cm}^{-1}$ suggests a chelating action of each terephthalate carboxylate group towards the manganese ion (cf. Scheme 1). The IR spectrum of **1** also showed a strong and broad O–H stretching band around 3,450 cm^{-1} confirming the presence of the coordinated water molecules. A $\mu_5\text{-}\kappa\text{O}:\kappa\text{O},\kappa\text{O}':\kappa\text{O}'':\kappa\text{O}''':\kappa\text{O}''''$ bridging action between five Mn atoms together with a $\mu_4\text{-}\kappa\text{O}:\kappa\text{O}':\kappa\text{O}'':\kappa\text{O}''''$ bridging action (Fig. 2) between four Mn atoms is known in the 3D coordination polymer $[\text{Mn}_3(\mu_5\text{-terephthalato})_2(\mu_4\text{-terephthalato})(\text{DEF})_2]_n$ (DEF = *N,N*-diethylformamide- κO) [35, 36]. The $\Delta\bar{\nu}$ value (269 cm^{-1}) in $[\text{Mn}(\mu\text{-ox})(\text{H}_2\text{O})_2]_n$ (**2**) (ox = oxalate, $^-\text{O}_2\text{C}-\text{CO}_2^-$) is much greater than in the ionic complexes, so the oxalate ligand in **2** forms bridges where each O atom from a carboxylate group coordinates to a Mn atom (Scheme 1). Numerous 2D (mixed-metal) manganese–oxalate coordination networks with a $\kappa\text{O},\kappa\text{O}'':\kappa\text{O}',\kappa\text{O}''''$ bridging mode (Fig. 2) between two metal atoms are known. These oxalate networks often have $\text{Mn}_2(\text{ox})_3$ or $\text{MnM}'(\text{ox})_3$ stoichiometry



Scheme 1

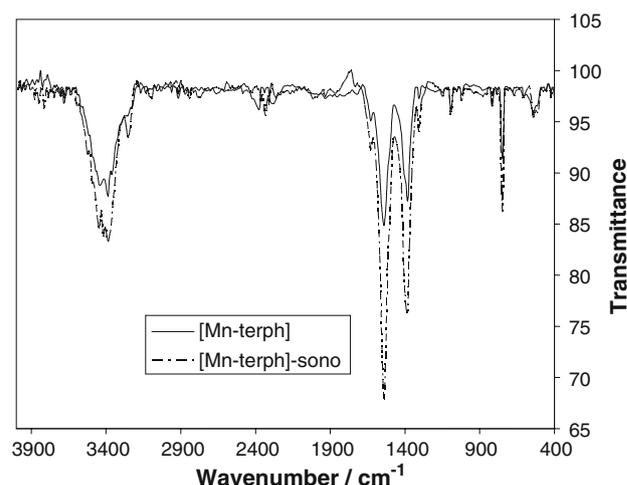


Fig. 1 IR spectra of compound **1** prepared as **1-bulk** and by sonication as **1-sono**

and carry a doubly negative charge per network formula unit so that counteranions, for example protonated amines [37], $[\text{M}(\text{bipy})_3]^{2+}$ [38–40], or alkali cations [41–45], are present. More rare examples of neutral 1D manganese–oxalato chains are catena-[diaqua(μ -oxalato- $\kappa\text{O},\kappa\text{O}'':\kappa\text{O}',\kappa\text{O}''''$)]purinemanganese(II), catena-[diaqua(μ_2 -oxalato- $\kappa\text{O},\kappa\text{O}'':\kappa\text{O}',\kappa\text{O}''''$)]adeninemanganese(II) [46], and catena-[aquaoxalato(propane-1,3-diamine)copper(II)][diaqua-(μ_2 -oxalato- $\kappa\text{O},\kappa\text{O}'':\kappa\text{O}',\kappa\text{O}''''$)]manganese(II) dihydrate [47]. The $\Delta\bar{\nu}$ value in $[\text{Mn}(\mu\text{-tart})]_n$ (**3**) (tart = D(–)-tartrate) of 185 cm^{-1} is greater than those of chelating carboxylate groups and close to the ionic value of $\Delta\bar{\nu} = 164 \text{ cm}^{-1}$ for the acetate ion. It is concluded that tartrate behaves as bis-monodentate bridging ligand in **3**. A known manganese–tartrate 1D coordination polymer exhibits a catena-[diaqua(μ_4 -tartrato- $\kappa\text{O}:\kappa\text{O}'':\kappa\text{O}'':\kappa\text{O}''''$)]

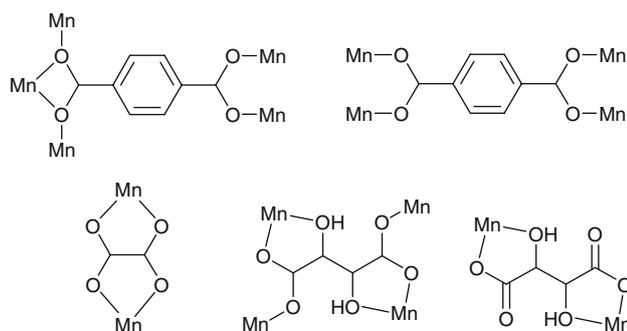


Fig. 2 Structurally authenticated dicarboxylate bridging actions in Mn-terephthalate, Mn-oxalate or Mn-tartrate coordination polymers

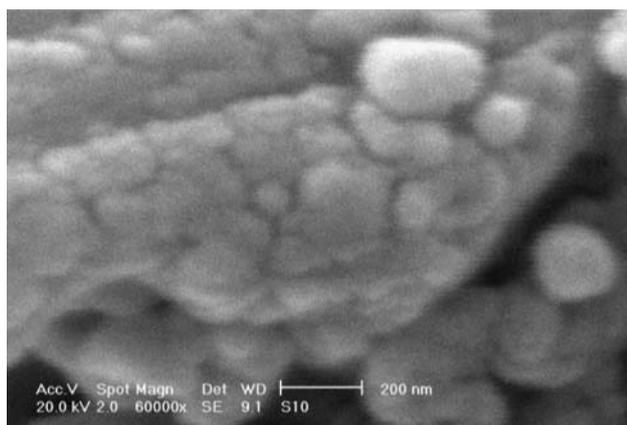


Fig. 3 SEM image of nanoparticles of **1-sono** produced by sonication

$\kappa O''$)(μ_2 -tartrato- $\kappa O:\kappa O''$)dimanganese(II)] motif (Fig. 2). Beside the noted carboxylate coordination in this polymer all C–OH groups are also bound to Mn so that a five-membered chelate ring through (H)O–C–C–O[−] coordination is formed with each Mn atom [48]. Because numerous attempts to crystallize compounds **1–3** have been unsuccessful, we have no structure elucidation based on single-crystal X-ray studies; proposed structures are given in Fig. 2.

Compounds **1**, **2**, and **3**, like coordination polymers, are not markedly soluble in the solvents CCl₄, CHCl₃, THF, CH₃CN, CH₃CH₂OH, CH₃OH, ethyl acetate, DMF, and water.

The particles in **1-sono** were characterized by scanning electron microscopy (SEM). Figure 3 shows the SEM image of **1-sono** with particle sizes ranging from 60 to 100 nm. In Fig. 4 the X-ray diffraction patterns of **1-bulk** and **1-sono** are shown to match with a little shift of the peaks.

From identical thermal gravimetric (TG) and differential thermal analyses (DTA) between 30 and 700 °C compounds **1-bulk** and **1-sono** are stable up to 115 °C, where the two H₂O molecules are removed (observed 14.4, calcd. 14.1%). At 390 °C the remaining organic terephthalate

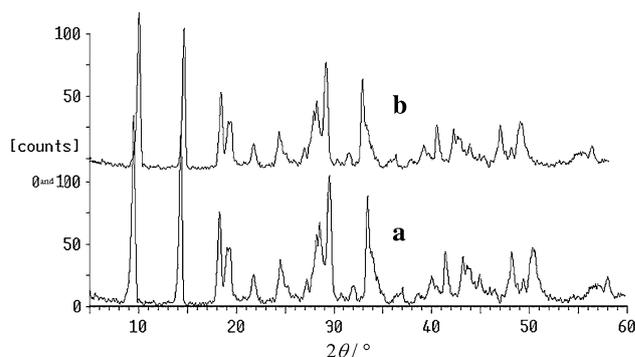


Fig. 4 X-ray diffraction pattern of (a) **1-bulk** and (b) **1-sono**

residue is lost (obs. 66.7, calcd. 64.3%), probably leaving Mn (obs. 18.9, calcd. 21.5%).

Catalytic olefin epoxidation studies

The epoxidation of cyclooctene was carried out using hydrogen peroxide as oxidant in the presence of [Mn(μ -terph)(H₂O)₂]_n (**1**), [Mn(μ -ox)(H₂O)₂]_n (**2**) and [Mn(μ -tart)]_n (**3**). In a search for suitable reaction conditions to achieve the maximum conversion, the effects of solvent, co-catalyst concentration, reaction temperature, and pre-catalyst nature were studied.

A series of blank experiments (Table 1) revealed that the presence of pre-catalysts **1**, **2**, or **3** and H₂O₂ oxidant are essential for an effective catalytic reaction. The system is unaffected by changing the order of addition. The only product of oxidation of cyclooctene was the epoxide cyclooctene oxide. No oxidation product was obtained in the absence H₂O₂ (entries 1 and 2 in Table 1), and in the absence of pre-catalysts **1**, **2**, or **3** the conversion of cyclooctene was only 9% after 24 h (entry 3 in Table 1). We have also noticed that the conversion of cyclooctene is

Table 1 Experiments on catalytic oxidation of cyclooctene to the epoxide

No.	Pre-catalyst	Co-catalyst	Oxidant	Conversion (%)	Time (h)
1	1-bulk	Imidazole	None	0	4
2	1-bulk	Imidazole	None	0	24
3	None	Imidazole	H ₂ O ₂	0	4
4	None	Imidazole	H ₂ O ₂	9	24
5	1-bulk	None	H ₂ O ₂	1	4
6	1-bulk	None	H ₂ O ₂	18	24
7	1-bulk	Imidazole	H ₂ O ₂	52	4
8	1-bulk	Imidazole	H ₂ O ₂	75	24

Reaction conditions: cyclooctene (0.11 g, 1 mmol), H₂O₂ (10 mmol), **1-bulk** (0.0039 mmol), acetonitrile (3 cm³), imidazole (0.097 mmol); temperature 60 ± 1 °C

greatly increased when a co-catalyst, for example imidazole, is added (entries 3 and 4 in Table 1). Studies of oxidation of cyclooctene with **1-bulk** in the presence of *tert*-butyl hydroperoxide gave only very low conversions after 24 h with vigorous stirring at 60 °C. No oxidation proceeds in the presence of air alone, that is, in the absence of hydrogen peroxide.

Coordination polymeric compounds **1**, **2**, and **3** are not heterogeneous catalysts but materials for the slow release of homogeneously active catalysts, as evidenced by the following series of experiments.

- 1 In the first experiment 0.0010 g **1** was used for epoxidation of cyclooctene with imidazole–H₂O₂ in 3 cm³ CH₃CN. After 24 h about half of the compound had dissolved, because only 0.0005 g could be recovered by filtration. Cyclooctene conversion was 75%;
- 2 In the second experiment the recovered 0.0005 g of **1** was used for oxidation of cyclooctene with imidazole–H₂O₂. After 24 h the same cyclooctene conversion of 75% as in the first experiment was obtained and the pre-catalyst **1** had almost completely dissolved;
- 3 In the third experiment the filtrate of the first experiment was used for catalysis. After addition of new cyclooctene–imidazole–H₂O₂ the reaction solution was stirred at 60 °C for 24 h. Cyclooctene conversion was again 75%.

Thus, compound **1** dissolves slowly under the oxidation reaction conditions. However, we exclude the possibility of leaching of “bare” Mn²⁺ ions from the coordination polymer into the solution, because hydrogen peroxide is decomposed very quickly by bare Mn²⁺ ions. It was verified that Mn²⁺ (added as MnCl₂·4H₂O–imidazole, Mn(O₂CCH₃)₂·4H₂O or Mn(O₂CCH₃)₂·4H₂O–imidazole) resulted in immediate (within 2–5 min) evolution of O₂, arising from hydrogen peroxide disproportionation, and no epoxide product was obtained. Such rapid H₂O₂ decomposition, evidenced by O₂ gas formation, was never observed with **1-bulk** or **1-sono** in the catalytic oxidation experiments. We therefore conclude that the dissolved catalyst species are carboxylate complexes of Mn(II).

The behavior of pre-catalytic compounds **1–3** as slow-release agents of catalytically active species is also reflected in the co-solvent, co-catalyst, and temperature dependence of the catalytic activity and the noteworthy induction period.

The effect of various co-solvents, for example carbon tetrachloride (dielectric constant $\epsilon = 2.2$), tetrahydrofuran ($\epsilon = 7.3$), ethanol ($\epsilon = 24.3$), acetonitrile ($\epsilon = 36.2$), and ethyl acetate ($\epsilon = 6$) on the epoxidation of cyclooctene with 35% aqueous hydrogen peroxide and **1-bulk** is shown in Fig. 5. It was observed that at 60 ± 1 °C catalytic activity decreases in the order acetonitrile > ethyl

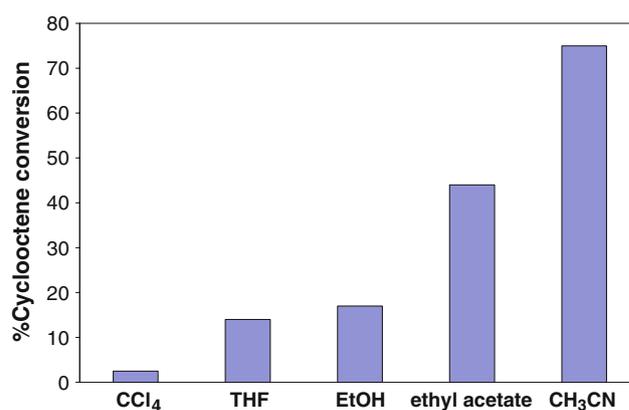


Fig. 5 Effect of solvent on the oxidation of cyclooctene to the epoxide by **1-bulk**. Reaction conditions: cyclooctene (1 mmol), **1-bulk** (0.001 g, 0.0039 mmol), imidazole (0.097 mmol), solvent (3 cm³), H₂O₂ (10 mmol); reaction times 24 h, temperature 60 ± 1 °C

acetate > ethanol > THF > carbon tetrachloride. The poor oxidation yield in CCl₄ is probably because of immiscibility of CCl₄ with H₂O₂. Because the amount of water and, therefore, its dielectric effect is constant in all solvent mixtures, we may focus only on co-solvent properties. The highest conversion in acetonitrile correlates with its large dielectric constant ($\epsilon = 36.2$), large dipole moment (3.92), and high boiling point (81.6 °C). When acetonitrile was replaced by ethyl acetate, conversion decreased from 52 to 41% after 4 h. Thus, a polar aprotic co-solvent such as acetonitrile with medium coordinating ability is the best medium for the manganese catalyst.

Also, the presence of a nitrogen base, for example imidazole, as a co-catalyst increased the conversion of cyclooctene. The effect of imidazole concentration on the oxidation of cyclooctene is illustrated in Fig. 6. Different imidazole-to-pre-catalyst molar ratios (20:1, 30:1, and 40:1) were considered while keeping the amount and concentration of cyclooctene (1 mmol) and pre-catalyst **2** (0.001 g, 0.0039 mmol) constant in 3 cm³ of acetonitrile at 60 ± 1 °C. When the imidazole-to-catalyst ratio was increased from 20:1 to 40:1 the conversion decreased, although it was still higher than without the co-catalyst. We used an imidazole-to-pre-catalyst molar ratio of 25:1 in further studies. The significant effect of imidazole as a co-catalyst in increasing substrate oxidation by non-heme systems has been reported [49]. Imidazole is a far better co-catalyst than Et₃N and pyridine. This reflects its better π -donor ability and coordination of imidazole with the Mn atom. The effect of such ligands in improving Mn–porphyrin mediated epoxidation is especially noteworthy [50–52]. A drawback to the use of nitrogen axial ligand effects is their oxidation. Imidazole is oxidized in the oxidation medium. For that reason excess imidazole was used

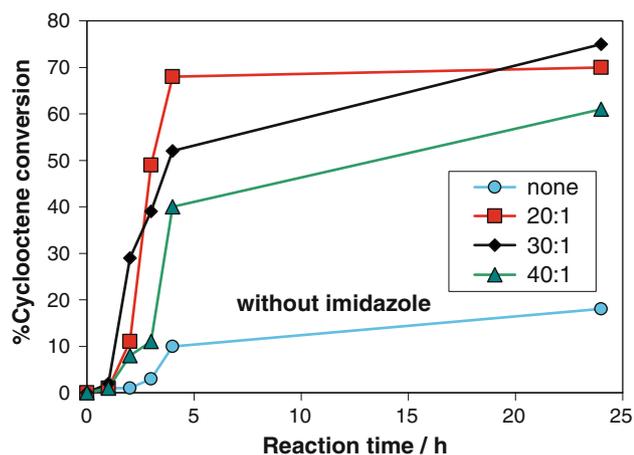


Fig. 6 Effect of imidazole concentration on oxidation of cyclooctene to the epoxide by **1-bulk**. Reaction conditions: cyclooctene (1 mmol), **1-bulk** (0.001 g, 0.0039 mmol), acetonitrile (3 cm³), H₂O₂ (10 mmol); temperature 60 ± 1 °C

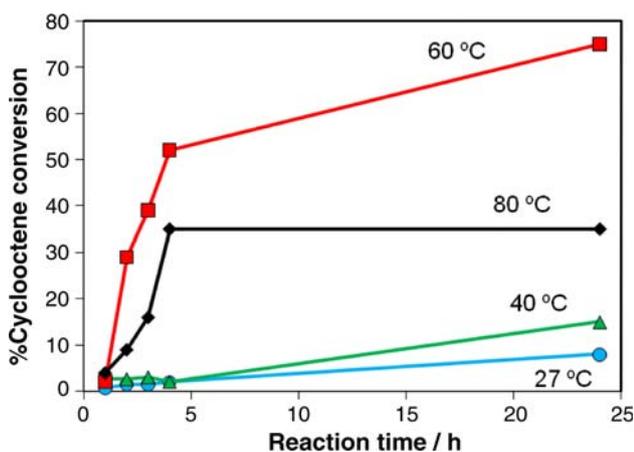


Fig. 7 Effect of reaction temperature on the conversion of cyclooctene to the epoxide by **1-bulk**. Reaction conditions: cyclooctene (1 mmol), **1-bulk** (0.001 g, 0.0039 mmol), imidazole (0.098 mmol), acetonitrile (3 cm³), H₂O₂ (10 mmol)

(imidazole-to-pre-catalyst molar ratios of 25:1). Pyridine can be oxidized by Mn–porphyrin catalytic systems containing iodosylbenzene [53].

The catalytic activity of **1-bulk** depends on the temperature. As shown in Fig. 7, the conversion of cyclooctene increased with temperature from 27 to 60 °C and then decreased again at 80 °C. At 60 °C a maximum conversion of 75% was obtained after 24 h.

The activities of the three pre-catalysts **1-bulk**, **2**, and **3** under the optimized conditions for catalyst **1-bulk** (acetonitrile solvent, imidazole-to-catalyst ratio = 25:1, reaction temperature 60 °C) are in the order of **3** < **2** < **1**, as illustrated in Fig. 8. Pre-catalyst **3** has the lowest activity (33%) and pre-catalyst **1-bulk** the highest (74%). Reducing the particle size of **1-bulk** by using the system **1-sono**

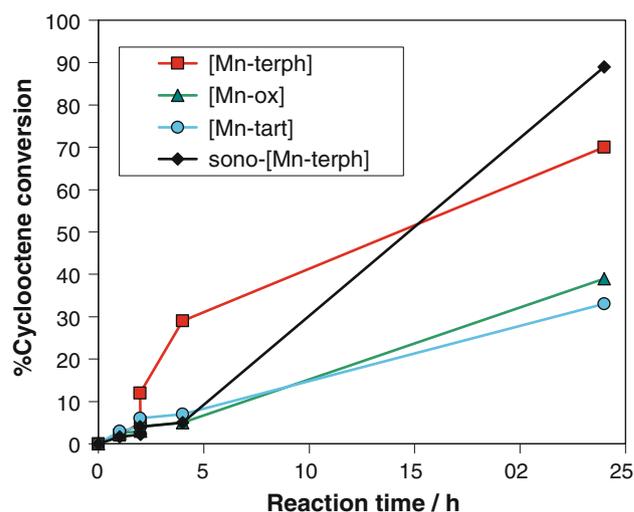


Fig. 8 Effects of the nature of the pre-catalyst on oxidation of cyclooctene to the epoxide. Reaction conditions: cyclooctene (1 mmol), H₂O₂ (10 mmol), pre-catalyst (0.0039 mmol), acetonitrile (3 cm³), imidazole (0.098 mmol); temperature 60 ± 1 °C

increased the conversion of cyclooctene further to 89%. However, **1-sono** has a longer induction time. Its increased activity is only evident at prolonged reaction times. It seems that the particles of **1-sono** become well dispersed in acetonitrile after 10–15 h of magnetic stirring. Then it has the highest catalytic activity in the oxidation of cyclooctene by H₂O₂.

Oxidation of various olefins was examined using the catalyst **1-bulk**. Results of these studies are summarized in Table 2. Small cyclic olefins such as cyclooctene and cyclohexene were converted to the corresponding epoxides with good yields (75 and 64%) and 100% selectivity. A regioselective effect of **1-bulk** was revealed by the preferential oxidation of norbornene to *exo*-norbornene oxide (21%) compared with the *endo* product (12%). For electron-poor olefins the oxidation proceeded with lower conversion than for cyclooctene and cyclohexene. Thus, the conversions of olefins with aryl substituents, i.e. indene, and *cis* and *trans*-stilbenes, were lower than for aliphatic olefins. Yet *cis*-stilbene was oxidized with 78% retention of configuration (7% *cis*-stilbene oxide compared with 2% *trans*-stilbene oxide). These results reflect some selectivity of **1** in the oxidation of small olefins with alkyl substituents.

The results of the oxidation of cyclooctene, cyclohexene, and *cis*-stilbene by various Mn(II) complexes and H₂O₂ are summarized in Table 3. Pyridine derivatives of TACN complexes of manganese(II) for olefin epoxidation with H₂O₂ are very active, but the ligands are expensive and difficult to prepare. Epoxide yields of olefin oxidation by the catalyst **1-bulk**–H₂O₂ system are sometimes better and mostly comparable with the results of the oxidation by

Table 2 Oxidation of various olefins by **1-bulk**

No.	Olefin	Product	Yield (%)	Time (h)
1	Cyclooctene	Cyclooctene oxide	52	4
2	Cyclooctene	Cyclooctene oxide	75	24
3	Cyclohexene	Cyclohexene oxide	53	4
4	Cyclohexene	Cyclohexene oxide	64	24
5	Norbornene	<i>exo</i> -Norbornene oxide	13	4
		<i>endo</i> -Norbornene oxide	7	
6	Norbornene	<i>exo</i> -Norbornene oxide	21	24
		<i>endo</i> -Norbornene oxide	12	
7	Indene	Indene oxide	–	4
8	Indene	Indene oxide	6.5	24
9	<i>trans</i> -Stilbene ^a	<i>trans</i> -Stilbene oxide	3	4
10	<i>trans</i> -Stilbene ^a	<i>trans</i> -Stilbene oxide	7	24
11	<i>cis</i> -Stilbene ^a	<i>cis</i> -Stilbene oxide	2	4
		<i>trans</i> -Stilbene oxide	1.5	
12	<i>cis</i> -Stilbene ^a	<i>cis</i> -Stilbene oxide	7	24
		<i>trans</i> -Stilbene oxide	2	

Reactions condition: cyclooctene (0.11 g, 1 mmol), H₂O₂ (10 mmol), catalyst **1** (0.0039 mmol), acetonitrile (3 cm³), imidazole (0.098 mmol); temperature 60 ± 1 °C

^a Reaction product(s) analyzed by ¹H NMR

H₂O₂ in the presence of sophisticated Mn(II) complexes (Table 3). In addition to the chemical simplicity and easy synthesis of the **1-bulk**-H₂O₂ system, it has the ability to somewhat limit the H₂O₂ disproportionation reaction which is characteristic of most Mn(II) compounds.

Conclusion

The Mn(II) dicarboxylate coordination polymers **1**, **2**, and **3** were prepared in water, and particles of **1** have also been synthesized by reaction of terephthalic acid and MnCl₂·4H₂O by a sonochemical method. The catalytic potential of these coordination polymers was tested in the oxidation of cyclooctene to the epoxide in acetonitrile, using hydrogen peroxide as oxygen source. Pre-catalytic compounds **1–3** behave as slow-release agents of catalytically active species under the reaction conditions. For compound **1** the catalytic activity was found to increase with the dielectric constant, dipole moment, and boiling point of the solvent (being highest in acetonitrile), with the reaction temperature to a maximum at 60 °C, and with an imidazole co-catalyst (highest activity found for a imidazole-to-**1** molar ratio of 20:1). Good activity with more than 64% conversion in 24 h was obtained for epoxidation of cyclooctene and cyclohexene, whereas aryl-substituted olefins gave only low yields. Some *exo* versus *endo* regioselectivity was found for norbornene. Of particular

interest is the ability of the coordination polymers to somewhat limit the H₂O₂ disproportionation reaction, which is characteristic of most Mn(II) compounds, and also the chemical simplicity of the pre-catalyst [7].

Experimental

Instrumentation

The reaction products of the catalytic oxidation were analyzed with an HP Agilent 6890 gas chromatograph equipped with an HP-5 capillary column (phenylmethylpolysiloxane, 30 m × 320 μm × 0.25 μm) and a flame-ionization detector (FID) and with a gas chromatography–mass spectrometer (Hewlett-Packard 5973 Series). ¹H NMR spectra were recorded with a Bruker 250-MHz spectrometer. Atomic absorption spectroscopy was carried out with a Varian 220 FS spectrophotometer. A multiwave ultrasonic generator (Sonicator-3000; Misonix, Farmingdale, NY, USA), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 600 W, was used for the ultrasonic irradiation. Microanalyses were carried out using a Heraeus CHN-O-Rapid analyzer, and the results agreed well with calculated values. Melting points were measured on an Electrothermal 9100 apparatus. The thermal behavior was measured with a PL-STA 1500 apparatus. IR spectra were recorded using Perkin-Elmer 597 and Nicolet 510P spectrophotometers.

The crystallite sizes of selected samples were estimated using the Scherrer equation [60] from the half-width of the diffraction peaks. The samples were characterized with a scanning electron microscope with gold coating.

Materials

Manganese(II) chloride tetrahydrate, terephthalic acid, oxalic acid, D-(–)-tartaric acid, and olefins were purchased from Merck and Fluka and used as received. Solvents of the highest grade commercially available (Merck) were used without further purification. Hydrogen peroxide (35% in water) was purchased from Fluka and its concentration (11.0 mol/dm³) was determined by the standard procedure [61].

Poly[diacquamanganese(II)(μ-terephthalate)] (**1**)

Synthesis of 1-bulk: A terephthalate solution was prepared by adjusting the pH of 1.118 g terephthalic acid (6.70 mmol) in 100 cm³ water to pH 7 with Et₃N. A solution of 1.034 g MnCl₂·4H₂O (5.00 mmol) in 10 cm³ water was added to the terephthalate solution and the resulting mixture was heated under reflux in air for 14 h.

Table 3 Comparison of the activity of Mn(II) complexes in the epoxidation of olefins with H₂O₂

Olefin	Mn(II) complex ^a	Additive	Yield (%)	Ref.
Cyclooctene	[Mn(μ -terph)(H ₂ O) ₂] _n , (1-bulk)	Imidazole	75	This study
Cyclooctene	[Mn(OTf) ₂ (^{H,Me} PyTACN)] and [Mn(OTf) ₂ (BPMCn)]	–	95–97	[11]
Cyclooctene	MnSO ₄	NaHCO ₃	67	[8, 54]
Cyclooctene	Polyoxometallate [WZnMn ₂ (ZnW ₉ O ₃₄) ₂] ¹²⁻	–	46	[55]
Cyclooctene	(β -F ₈ TPFPP)Mn	CH ₃ CO ₂ NH ₄	32	[56]
Cyclooctene	Mn ₂ L _a	CH ₃ COONH ₄	71	[57]
	Mn ₂ L _a ·SiO ₂		73	
	Mn ₂ L _b		71	
	Mn ₂ L _b ·SiO ₂		72	
	Mn ₂ L _c		71	
	Mn ₂ L _c ·SiO ₂		65	
Cyclooctene	Mn(II)(PFTDCCl ₈ PP)	Imidazole	7 ^b	[58]
	Si-MnPFTDCCl ₈ PP	Imidazole	7 ^b	
Cyclooctene	MnClSaloph with 7-22 Equiv. H ₂ O ₂	1,5-Dicyclohexyl-imidazole (DCI)	78	[59]
Cyclohexene	[Mn(μ -terph)(H ₂ O) ₂] _n , (1-bulk)	Imidazole	64	This study
Cyclohexene	MnSO ₄	NaHCO ₃	84	[8, 44]
Cyclohexene	Polyoxometallate [WZnMn ₂ (ZnW ₉ O ₃₄) ₂] ¹²⁻	–	29	[55]
Cyclohexene	(β -F ₈ TPFPP)Mn	CH ₃ CO ₂ NH ₄	9	[56]
Cyclohexene	Mn ₂ L _a	CH ₃ COONH ₄	57	[57]
	Mn ₂ L _a ·SiO ₂		68	
	Mn ₂ L _b		41	
	Mn ₂ L _b ·SiO ₂		64	
	Mn ₂ L _c		42	
	Mn ₂ L _c ·SiO ₂		36	
<i>cis</i> -Stilbene	[Mn(μ -terph)(H ₂ O) ₂] _n , (1-bulk)	Imidazole	<i>cis</i> -/ <i>trans</i> - epoxide 7:2	This study
<i>cis</i> -Stilbene	Mn ₂ L _a	CH ₃ COONH ₄	32	[57]
	Mn ₂ L _a ·SiO ₂		17	
	Mn ₂ L _b		16	
	Mn ₂ L _b ·SiO ₂		16	
	Mn ₂ L _c		52	
	Mn ₂ L _c ·SiO ₂		60	

^a ^{H,Me}PyTACN, BPMCN = pyridine derivatives of TACN (1,4,7-triazacyclononane), β -F₈TPFPP = β -octafluoro-*meso*-tetrakis(pentafluorophenyl)porphyrin, L_a = 4-[2-[2-(1,1,1,5,5,5-hexafluoro-4-oxopentylideneamino)ethylamino]ethylimino]-1,1,1,5,5,5-hexafluoropentan-2-one, L_b = 4-[2-[2-(5,5,5-trifluoro-4-oxopentylideneamino)ethylamino]ethylimino]-1,1,1-trifluoropentan-2-one, L_c = 3-[2-[2-(3-hydroxy-1,3-diphenylallylideneamino)ethylamino]ethylimino]-1,3-diphenylpropen-1-ol, PFTDCCl₈PP = β -octachloro-5-(pentafluorophenyl)-tris(2,6-dichlorophenyl)porphyrin, Saloph = salophen

^b Yields based on H₂O₂

The white precipitate which formed was then isolated by filtration, washed with water, and air dried (yield 1.027 g, 81%). IR (KBr): $\bar{\nu}$ = 3,450 (s, br), 1,546 (vs), 1,392 (vs), 1,100 (w), 823 (w), 754 (s), 554 (m, br) cm⁻¹.

Synthesis of *1-sono*: A high-density ultrasonic probe was immersed directly into a solution of 1.118 g terephthalic acid (6.70 mmol) in 100 cm³ water adjusted to pH 7 with Et₃N. A solution of 1.034 g MnCl₂·4H₂O (5.00 mmol) in 10 cm³ water was then added dropwise. The solution was ultrasonically irradiated with a power of 18 W for 1 h. The

precipitate obtained was isolated by filtration, washed with doubly distilled water, and air-dried (yield 1.091 g, 85%). IR (KBr): $\bar{\nu}$ = 3,392 (s, br), 1,539 (vs), 1,385 (vs), 1,092 (w), 815 (w), 746 (s), 538 (m, br) cm⁻¹.

Poly[diaquamanganese(II)(μ -oxalate)] (**2**)

The synthetic procedure of **1** was followed by using 0.603 g oxalic acid (6.70 mmol) instead of terephthalic acid. Yield: 0.626 g (50%). IR (KBr): $\bar{\nu}$ = 3,392 (vs, vb), 1,638 (vs, b), 1,369 (m), 1,315 (s), 1,100 (w), 823 (m), 738 (w), 500 (m) cm⁻¹.

Poly[manganese(II)(μ -D-tartrate)] (3)

The synthetic procedure for **1** was followed by using 1.006 g D-(–)-tartaric acid (6.70 mmol) instead of terephthalic acid. Yield: 0.157 g (37%). IR (KBr): $\bar{\nu}$ = 3,377 (s, vb), 2,969 (w), 1,608 (vs), 1,423 (vs), 1,377 (s), 1,238 (w), 1,092 (s), 1,046 (m), 746 (m), 638 (s), 485 (m) cm^{-1} .

Oxidation of cyclooctene, general procedure

Oxidation reactions were performed in a stirred round-bottomed flask fitted with a water-cooled condenser. Reactions were carried out under atmospheric pressure in air in an oil bath at 60 ± 1 °C with acetonitrile as co-solvent and aqueous H_2O_2 (35%) as oxidant. Typically, 0.004 mmol of catalyst, 0.098 mmol of imidazole, 1.0 mmol of olefin, and 3 cm^3 acetonitrile were added to the flask. After the mixture had been heated to 60 ± 1 °C, an aqueous solution (1.0 cm^3 , 11.0 mmol) of H_2O_2 was added. After the required time, the products were analyzed by gas chromatography, gas chromatography–mass spectrometry, and ^1H NMR spectrometry. To ensure reproducibility, the oxidation experiments with H_2O_2 in the different solvents with **1-bulk** at 60 °C and a reaction time of 24 h (cf. Fig. 5) were each repeated ten times (conversions for single experiments varied within $\pm 2\%$). The conversion percentage given in Fig. 5 is an average value from these ten experiments. Excess H_2O_2 was slowly decomposed to H_2O and O_2 during the oxidation reaction.

In the oxidation of *cis* and *trans*-stilbenes, the reaction was followed by ^1H NMR after 4 and 24 h, in which ^1H NMR spectra of the crude products were acquired. For *cis*-stilbene, no traces of *trans*-stilbene were observed. These findings confirmed that *cis*-stilbene is stable in the oxidation reaction medium and does not isomerize to *trans*-stilbene.

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