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Heterotrinuclear manganese(II) and vanadium(IV) Schiff base complexes as epoxidation catalysts

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Abstract The catalytic epoxidation of styrene using urea-hydrogen peroxide and heterotrinuclear Cu(II) complexes with general formula $(ML^n)_2Cu(acac)_2$, where $n = 1$–3 and $M = VO^{2+}$ or Mn^{2+} is reported. Schiff base complexes ML^n involving a 3,4-diaminopyridine bridge with free coordination site were used as the ligand, where $(L^n)^{2-}$ is $[(5\text{-x-Sal})_2Py]^2$ and x = H, Br or NO_2. The complexes were characterized by physico-chemical and spectroscopic methods. The electrochemical properties of M were modified upon trinuclear complex formation. The trinuclear complexes show high catalytic activity, with up to 86% conversion and 93% selectivity, while no catalytic properties were observed for the monomeric complexes. The catalyst could be reused with some loss of activity.

Introduction

Controlled epoxidation of alkenes with stable and efficient catalysts using environmental friendly oxidants is an important goal. In recent years, styrene oxide has been used as a starting material for epoxy resins, flavoring agents in food, tobacco, soap, cosmetic essences, perfumes, and pharmaceuticals [1, 2]. Since the first epoxidation of allylic alcohols by Sharpless [3], various manganese Schiff base catalysts have been developed using different oxygen sources such as iodosylbenzene, sodium hypochlorite, hydrogen peroxide [4], alkyl hydroperoxide [5, 6], molecular oxygen [7], and more recently urea-hydrogen peroxide (UHP) [8–11]. UHP is a readily available derivative of H_2O_2 that releases H_2O_2 into solution in a controlled manner, and has been used as oxidant in the presence of a transition metal complex catalyst [8].

Manganese complexes are less environmentally damaging than those of other transition metals, and are also involved in many biological processes. Therefore, many manganese complexes of porphyrin, phthalocyanine, triazamacrocycle, and Schiff base ligands have been synthesized as mimics of enzymes in connection with oxidation state, coordination number, and number of manganese sites [12]. Also, the ability of the copper(II) to accommodate different geometries and coordination numbers can lead to structural diversity and variations in physico-chemical properties of its heterometallic complexes.

Heteropolymetallic complexes are of current interest due to their importance in the study of charge transfer between metal centers [13], in catalysis and molecular recognition [14], and in the area of bioinorganic chemistry for their potential use as bio-mimetics for the active sites of many metalloproteins [15–17], especially when the bridging group between the metal atoms is of biological relevance, such as imidazolate, carboxylate, etc. A large number of homo-metallic complexes have been described [18–20], but hetero-metallic compounds with Schiff base ligands are still limited in number [21–23]. To our knowledge, no examples of trinuclear compounds ML–Cu–LM, where M = V(IV) or Mn(II), involving pyridine-bridges have been reported. A popular and successful two-step approach for the preparation of hetero-metallic systems is the metallo-ligand strategy, based on the interaction between a preformed complex possessing free coordination sites with a secondary metal [24].

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In this paper, the synthesis of new heterotrinuclear complexes **1–6** (Fig. 1), namely (ML^n)$_2$Cu(acac)$_2$, $n = 1$–3 and M = VO^{2+} or Mn^{2+}, involving unsymmetrical Schiff base ligands where (L^n)$^{2-}$ is [(5-x-Sal)$_2$Py]$^{2-}$, x = H, Br or NO$_2$ are reported. Preformed Schiff base complexes ML^n, **1a–6a** with a 3,4-diaminopyridine bridge and free coordination site were used. Compounds **1–6** have been studied as catalysts for epoxidation of styrene with UHP as primary oxidant at low temperature.

Results and discussion

Selective epoxidation reactions were typically performed according to the established procedure [25] using complexes **1–6** as catalysts, styrene as substrate, 1-methyl imidazole as co-catalyst, and UHP as primary oxidant. Mononuclear Schiff base complexes {Mn[(5-R-Sal)$_2$Py]}, {VO[(5-R-Sal)$_2$Py]}, (R = H, Br, NO$_2$) and the corresponding ligands were obtained according to previous procedures [5–7].

Trinuclear Schiff base complexes M–Cu–M, {M[(5-R-Sal)$_2$Py]$_2$Cu(acac)$_2$}, **1–6**, were prepared by mixing two equivalents of mononuclear Schiff base complexes {M[(5-R-Sal)$_2$Py]} with one equivalent of Cu(acac)$_2$ in refluxing ethanol. Similar treatment of three or four equivalent of {M[(5-R-Sal)$_2$Py]} afforded the same trinuclear compounds (Fig. 1). The products **1**, **2**, and **3** were isolated as dark brown, brown, and orange powders, respectively.

Spectroscopic and physico-chemical studies

In order to give an idea about the structures of the mononuclear metal complexes, {M[(5-R-Sal)$_2$Py]}, **1a–6a**, the main IR bands were compared with those of the free ligands [26]. A strong broad band observed at 3,447–3,135 cm^{-1} in the spectrum of the free ligand is assigned to νOH. A broad band in this range is also seen in the spectra of the manganese complexes, and in this case is attributed to waters of hydration or coordinated ethanol. The Schiff bases show the C=N imine band in the range 1,603–1,609 cm^{-1}. Upon coordination to the metal, a shift to lower wavenumber (1,594–1,606 cm^{-1}) was observed, consistent with coordination of the nitrogen. The phenolic C–O of the free ligands is observed around 1,273–1,285 cm^{-1}. Upon coordination, this band is shifted to lower wavenumber, suggesting coordination of the phenolic oxygen [27]. In the free ligand, a band observed at 980–993 cm^{-1} is ascribed to νC–H(CH=N). This band shifted to higher wave number upon complexation. New IR bands at 431–455 and 470–560 cm^{-1} in the spectra of the complexes are assigned to ν(M ← O) and ν(M ← N) vibrations [28], respectively. Hence, the IR spectra indicate that the Schiff bases act as dibasic tetradentate ligands towards the central metal atoms. The ν(C=N) bands of the pyridine moiety were unshifted in the spectra of the complexes.

The assignments of the important IR bands of the trinuclear complexes are recorded in Table 1. It can be seen that these Schiff base complexes exhibit an absorption at around 1,596–1,615 cm^{-1}, which is ascribed to the stretching vibration of the C=N(imine) band. The frequencies of this band are considerably lower than these of the C=N(pyridine) vibrations, and the C=N(imine) band also shows a stronger intensity. In the IR spectra of the trinuclear Schiff base complexes **1–6**, the pyridine C=N stretching vibrations at 1,632–1,680 cm^{-1}, are shifted by about 5–30 cm^{-1} compared to **1a–6a** [7], due to the strong inductive effect of the copper atom. Our efforts to prepare single crystals of these complexes for X-ray diffraction measurements have been unsuccessful.

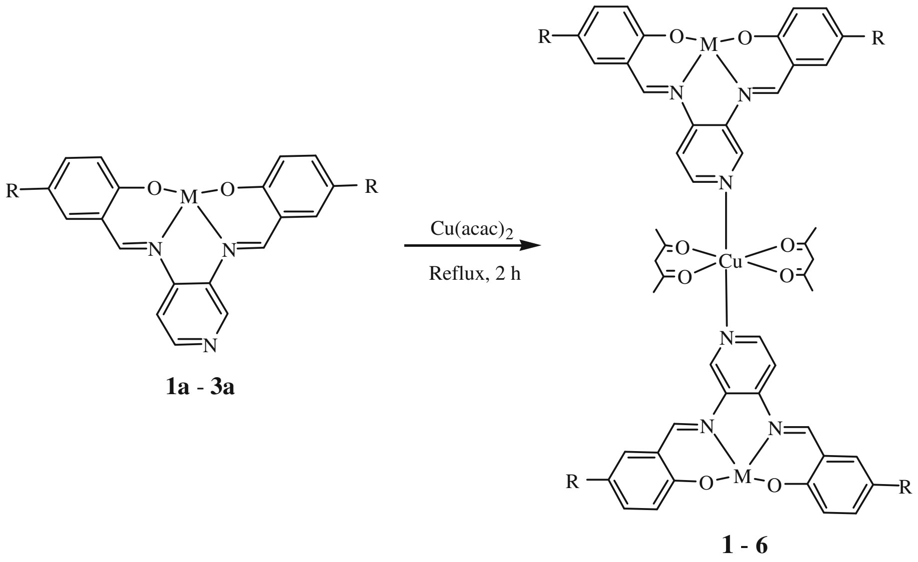


Fig. 1 Heterotrinuclear copper(II) complexes {M[(5-R-Sal)$_2$Py]}$_2$Cu(acac)$_2$, **1–6** where M = V^{IV}O or Mn^{II}. **1**, **1a**, M = Mn, R = H; **2**, **2a**, M = Mn, R = Br; **3**, **3a**, M = Mn, R = NO$_2$; **4**, **4a**, M = VO, R = H; **5**, **5a**, M = VO, R = Br; **6**, **6a**, M = VO, R = NO$_2$

Table 1 Selected IR bonds (cm^{-1}) and UV–Vis data (nm) for trinuclear complexes **1–6**

No.	Complex[a]	v(C = N)		v(M–N)	v(M = O)	λ, nm (ε, M^{-1} Cm^{-1})			
		Imine	Pyridine			$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	d → d	
1	{Mn[(5-H-Sal)$_2$Py]}$_2$Cu(acac)$_2$	1,603	1,632	549	–	233 (4,129)	–	386 (402)	465 (187), 742 (16)
2	{Mn[(5-Br-Sal)$_2$Py]}$_2$Cu(acac)$_2$	1,596	1,647	585	–	237 (4,430)	294 (1,449)	438 (290)	743 (49)
3	{Mn[(5-NO$_2$-Sal)$_2$Py]}$_2$Cu(acac)$_2$	1,601	1,680	562	–	–	291 (1,207)	363 (668)	408 (803), 725 (28)
4	{VO[(5-H-Sal)$_2$Py]}$_2$Cu(acac)$_2$	1,602	1,648	543	978	238 (4,288)	312 (2,025)	413 (1,369)	742 (49)
5	{VO[(5-Br-Sal)$_2$Py]}$_2$Cu(acac)$_2$	1,615	1,648	547	960	232 (9,430)	–	396 (385)	741 (18)
6	{VO[(5-NO$_2$-Sal)$_2$Py]}$_2$Cu(acac)$_2$	1,608	1680	519	950	232 (3,958	–	379 (416)	739 (19)

[a] In DMF solution

The V=O stretching frequencies of complexes **4–6** were observed between 950 and 978 cm^{-1} (Table 1). It has been reported that oxovanadium complexes with coordination number 5 have v(V=O) values at about 950–1,000 cm^{-1} [29]. Thus, the three vanadyl complexes should exhibit monomeric square-pyramidal geometries with no ligand in the axial position.

Bands between 434 and 498 cm^{-1} in the spectra of **1–6** can be assigned to v(Cu–N). It is apparent that chelation of the divalent copper to the ligand occurs through the pyridine nitrogen atom. The acetylacetonate ligands occupy the other coordination sites to complete the coordination sphere of the copper. Figure 1 shows the proposed structure of the trinuclear complexes. In the UV–Vis spectra, the Cu(II) complex has a band at 630–650 nm and a shoulder at 425–455 nm that could be assigned to LMCT.

The electronic spectral data of the manganese(II) and vanadyl complexes in DMF are summarized in Table 1. The transitions due to the organic ligands have higher ε_{max} values than the d–d transitions of the atoms. The bands observed for all the metal complexes at 233–291 nm and the shoulder at 294–312 nm were assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively, within the aromatic rings in the ligands. The absorption bands in the range 363–441 nm may be attributed to ligand-to-metal charge transfer by analogy with similar manganese complexes. The bands at 408–744 nm can be assigned to d–d transitions on the basis of their low extinction coefficients [30, 31].

Although the electronic spectra of the manganese complexes with multidentate Schiff base ligands are not in general a good indicator of their geometry, they can provide supporting information about the structure [32]. Complexes **1–3** display strong absorption bands at ca. 386 nm, which can be assigned to the charge transfer from the ligands to the Mn. The spectrum of compound **1** shows bands associated with d–d transitions at ca. 465 nm.

Molar conductivities of the complexes were measured in DMF (10^{-3} M solution) at room temperature and lie in the range of 7.23–14.02 Ω^{-1} cm^2 mol^{-1}, indicating that they are non-electrolytes [33]. As such, these complexes are likely neutral overall.

Electrochemical study of the complexes was performed using DMF as solvent at 25 °C under a nitrogen atmosphere using glassy carbon as the working electrode, Ag/AgCl as reference electrode, and tetrabutylammonium hexafluorophosphate as the supporting electrolyte at a scan rate of 100 mV/s. The results are summarized in Tables 2 and 3.

The cyclic voltammogram of compound **3** shows two reductive peaks at 320 and 482 mV due to the Mn(II)/Mn(III) redox couple, both of which are irreversible in nature. The observed potential gap (150 mV) between the two reductions indicates efficient communication between the Mn(III) centers through the Cu(II) bridge. Two oxidation responses are also expected for such a system, but only one such oxidation is observed at 612 mV, due to oxidation of Mn(III) to Mn(IV).

Catalytic epoxidation of styrene

Selective epoxidation reactions were investigated using the trinuclear complexes **1–6** as catalysts, styrene as substrate, UHP as oxidant, and in the case of manganese catalysts **1–3**, 1-methyl imidazole as co-catalyst. The oxidation

Table 2 Electrochemical results for mononuclear complexes **1a–6a**

Entry	Complex	Ep, mVΔ	E$_{pa}$, mV	E$_{pc}$, mV
1a	Mn[(5-H-Sal)$_2$Py]	–	1,039	–
2a	Mn[(5-Br-Sal)$_2$Py]	–	1,005	–
3a	Mn[(5-NO$_2$-Sal)$_2$Py]	–	1,104	–
4a	VO[(5-H-Sal)$_2$Py]	78	598	520
5a	VO[(5-Br-Sal)$_2$Py]	59	747	688
6a	VO[(5-NO$_2$-Sal)$_2$Py]	69	988	919

Electrochemical data were measured for 0.1 M of sample in DMF solution, 0.1 M of tetrabutylammonium hexaflourophosphate as supporting electrolyte. Potentials are reported versus AgCl/Ag as reference electrode at 100 mV/S Scan rate

Table 3 Electrochemical data for the trinuclear complexes **1**–**6**

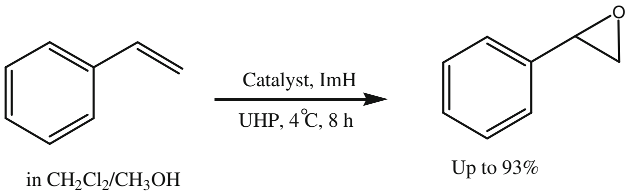
No.	Complex	E_{pc}, mV	E_{pa}, mV	Ep, mVΔ	$E_{1/2}$, mV
1	$\{Mn[(5\text{-}H\text{-}Sal)_2Py]\}_2Cu(acac)_2$	520	610	90	565
2	$\{Mn[(5\text{-}Br\text{-}Sal)_2Py]\}_2Cu(acac)_2$	480	592	112	536
3	$\{Mn[(5\text{-}NO_2\text{-}Sal)_2Py]\}_2Cu(acac)_2$	482	612	140	552
4	$\{VO[(5\text{-}H\text{-}Sal)_2Py]\}_2Cu(acac)_2$	450	625	175	527
5	$\{VO[(5\text{-}Br\text{-}Sal)_2Py]\}_2Cu(acac)_2$	695	790	95	752
6	$\{VO[(5\text{-}NO_2\text{-}Sal)_2Py]\}_2Cu(acac)_2$	707	802	95	760

Electrochemical data were measured for 0.1 M of sample in DMF solution, 0.1 M of tetrabutylammonium hexaflourophosphate as supporting electrolyte. Potentials are reported versus AgCl/Ag as reference electrode at 100 mV/S Scan rate

reactions were performed under previously optimized conditions, specifically catalyst/ImH/styrene/UHP (1:30:30:50) in a (1:1) mixture of CH_3OH/CH_2Cl_2. The yields remained constant upon further increasing of ImH up to 50 equivalents.

In addition, H_2O_2 was used as an oxidant for comparison with UHP (Scheme 1). For control experiments, epoxidations without any catalyst and with mononuclear metal complexes were run. GC analysis showed extremely low yields of styrene oxide in these control experiments; within 8 h almost no conversion occurred. This is not surprising for the mononuclear complexes, given their totally irreversible redox behavior.

As expected, on the basis of their CVs, the trinuclear complexes **1**–**6** exhibited catalytic activity toward conversion of styrene to styrene oxide. These catalytic activities are associated with the binding of copper between two metal complex centers, via the pyridine nitrogen atoms. To the best of our knowledge, there is no example in the literature of catalytic activity for pyridine bridged manganese or vanadyl Schiff base complexes. As mentioned above, the monomeric complexes **1a**–**6a**, show no catalytic activity. Interestingly, however, the analogous salophen complexes, in which pyridine is replaced by a simple benzene ring, do show catalytic activity. Using hydrogen peroxide as oxidant, conversions of 27 and 18% were obtained for manganese and vanadyl salophen complexes, respectively. Therefore, the results for trinuclear catalysts **1**–**6** suggest that the two metal centers are not working in isolation but have some cooperative interaction through the copper, and further, the pyridine bridge has lost its inhibitor activity due to coordination to copper.



Scheme 1 Catalytic oxidation of styrene

Using of H_2O_2, within 2 h, the conversion of styrene reached a maximum of 42% for **2**. When the reaction time was increased to 8 h, the conversion was a little changed and finally reached 50%. The vanadyl complexes **4**–**6** showed lower catalytic activity than the manganese complexes **1**–**3**. Figure 2 shows the correlation between the conversion and the reaction time, where the reaction temperature was fixed at 4 °C for **1**–**3,** using UHP or H_2O_2 as oxidants. Maximum styrene epoxide selectivity was 73 and 69% for **2** and **5**, respectively, for 8 h reaction time. Increasing the reaction time to 24 h gave 86% conversion of styrene for **2.**

Maximum conversion of styrene with UHP catalyzed by complex **2** was achieved at about 8 h with 48% conversion and 93% selectivity. In the case of the vanadyl complexes, both the conversion and selectivity were lower than the manganese complexes for a reaction temperature of 4 °C.

Using a co-catalyst such as imidazole is necessary for efficient alkene epoxidation; the imidazole acts as a proximal ligand to Mn in the presence of H_2O_2 or UHP [8–10, 34, 35]. Also, in the current catalytic system, the proximal effect of imidazole is much more important than its distal effect.

The catalyst solution was reused under the same epoxidation conditions, using the same amounts of styrene and UHP or H_2O_2. In all cases, conversion was decreased at about 25–36%, probably due to degradation of the catalyst. Further investigations are in progress to define the reaction mechanism, role of 1-methylimidazole and the reasons for loss of activity of the catalyst on reuse.

Experimental

Chemicals and solvents were obtained from Merck, apart from $VO(acac)_2$ and 2-hydroxybenzaldehyde which were obtained from Aldrich.

Infrared spectra were recorded on a Shimadzu IR 460 spectrophotometer using KBr pellets. Electronic absorption spectra were recorded on a Varian UV–Vis Cary 100E

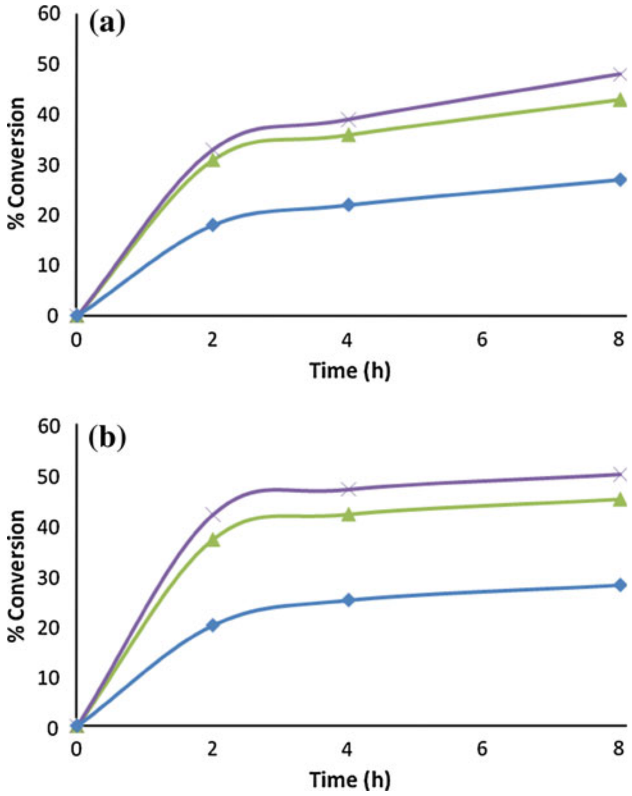


Fig. 2 Relationship between the conversion of styrene and the reaction time, where the reaction temperature was fixed at 4 °C and 1-methyl imidazole was used as co-catalyst for **1**–**3** using **a** UHP **b** H_2O_2 as oxidant. Triangles, complex **1**; cross, complex **2**; diamond, complex **3**

spectrophotometer. $^{1}H\{^{13}C\}$ NMR spectra were obtained on a Bruker FT-NMR AC-250 (250 MHz) spectrophotometer using TMS as internal standard and $CDCl_3$ and DMSO-d_6 as solvents. Elemental analyses (C, H, N) were obtained using a Heraeus Elemental Analyzer CHN-O-Rapid (Elemental Analyses system, GmbH-West Germany). Melting points were determined with a B-540 Buchi melting point apparatus. Cyclic voltammograms (CVs) were obtained using an electrochemical system (Palm Sense, The Netherlands) in conjunction with a three-electrode system and a personal computer for data storage and processing. An Ag/AgCl (3 M KCl) reference electrode, a Pt wire (counter electrode) and a glassy carbon working electrode were employed for the electrochemical studies. Voltammetric measurements were performed at room temperature in DMF solution with 0.1 M tetrabutylammonium hexaflourophosphate as the supporting electrolyte. Gas chromatography analyses were obtained on an Agilent instrument 6,890 N equipped with an FID detector and a capillary column (30 m × 0.25 mm × 0.01 mm), 5% phenyl methyl siloxane, and hydrogen as carrier gas.

Preparation of the mononuclear Schiff bases complexes $\{Mn[(5\text{-}R\text{-}Sal)_2Py]\}$ and $\{VO[(5\text{-}R\text{-}Sal)_2Py]\}$

Schiff base complexes **1a**–**6a** were obtained by previously reported methods [4–7, 25]. Synthetic procedures and characterization data are provided in the supporting information.

Synthesis of $\{Mn[(5\text{-}R\text{-}Sal)_2Py](EtOH)\}_2Cu(acac)_2$

To a stirred and hot solution of $Cu(acac)_2$ (0.261 g, 1 mmol) in ethanol (40 ml) was added a hot solution of $Mn[(5\text{-}R\text{-}Sal)_2Py]$ (**1a**–**3a**) (2 mmol), in ethanol (30 ml). The color of the solution changed after a few minutes. The reaction mixture was then refluxed for 120 min. The solution was concentrated and cooled to yield a brown precipitate. This was filtered off, washed with diethyl ether, dried at 60 °C overnight, and then recrystallized from ethanol until a pure product was obtained. Yields 70–75%. Elemental analysis results for **1**: found(%) C, 56.8; H, 4.7; N, 8.0; Cu, 5.4; Mn, 10.3. Calc. for $C_{52}H_{54}CuMn_2N_6O_{10}$: C, 57.0; H, 5.0; N, 7.7; Cu, 5.8; Mn, 10.0%. For **2**: found C, 44.0; H, 3.4; N, 6.2; Cu, 4.7; Mn, 8.0. Calc. for $C_{52}H_{50}Br_4CuMn_2N_6O_{10}$: C, 44.2; H, 3.6; N, 6.0; Cu, 4.5; Mn, 7.8%. For **3**: found C, 48.6; H, 3.7; N, 11.2; Cu, 5.3; Mn, 9.0. Calc. for $C_{52}H_{50}CuMn_2N_{10}O_{18}$: C, 48.9; H, 4.0; N, 11.0; Cu, 5.0; Mn, 8.6%.

Synthesis of $\{VO[(5\text{-}R\text{-}Sal)_2Py]\}_2Cu(acac)_2$

To a stirred and hot solution of $Cu(acac)_2$ (0.261 g, 1 mmol) in ethanol (40 ml) was added a hot solution of $VO[(5\text{-}R\text{-}Sal)_2Py]$ (2 mmol), in ethanol (30 ml). The color of the solution changed after a few minutes. The reaction mixture was then refluxed for 120 min. The solution was concentrated and cooled to yield a light brown precipitate, which was filtered off, washed with diethyl ether and dried at 60 °C overnight. The product was recrystallized from ethanol. Yields 70–75%. Elemental analysis results for **4**: found (%) C, 56.2; H, 4.4; N, 7.9; Cu, 6.4; V, 9.7. Calc. for $C_{48}H_{42}CuN_6O_{10}V_2$: C, 56.1; H, 4.1; N, 8.2; Cu, 6.2; V, 9.9%. For **5**: found C, 42.7; H, 3.1; N, 6.0; Cu, 5.0; V, 7.3. Calc. for $C_{48}H_{38}Br_4CuN_6O_{10}V_2$: C, 42.9; H, 2.8; N, 6.2; Cu, 4.7; V, 7.6%. For **6**: found C, 47.9; H, 2.9; N, 11.9; Cu, 5.4; V, 8.1. Calc. for $C_{48}H_{38}CuN_{10}O_{18}V_2$; C, 47.7; H, 3.2; N, 11.6; Cu, 5.3; V, 8.4%.

Catalytic epoxidation of styrene

(a) Using H_2O_2: To a stirred solution of 0.01 mmol catalysts, **1**–**6**, in DMF, 3 mL of 0.1 M $NaHCO_3$ and 0.3 mmol styrene was added at 2–4 °C under argon. For the manganese catalysts, 0.03 mol 1-methylimidazole

Table 4 Epoxidation of styrene using complexes **1**–**6** as catalyst

Complex	UHP/conversion (%)			Selectivity to epoxide	H_2O_2/conversion (%)			Selectivity to epoxide
	2 h	4 h	8 h		2 h	4 h	8 h	
1	31	36	43	89	37	42	45	68
2	33	39	48	93	42	47	50	73
3	18	22	27	71	20	25	28	53
4	–	–	30	64	–	–	29	60
5	–	–	34	75	–	–	30	69
6	–	–	18	43	–	–	20	42[a]
Without catalyst	–	–	<5	<1	–	–	<5	<1

For the manganese catalysts, 1-methyl imidazole was added as co-catalyst

The selectivity was calculated on the basis of epoxide yield/conversion ratio

[a] Other major styrene oxides, benzaldehyde [36], and phenylacetaldehyde [37], were determined qualitatively as by products

was also added. After 15 min stirring, 1 mmol hydrogen peroxide 30% was added dropwise. The reaction mixture was stirred for 8 h at room temperature. The progress of the reaction was monitored by periodic sampling for GC determination. Chlorobenzene was used as standard.

(b) Using urea-hydrogen peroxide (UHP): To a stirring solution of 0.01 mmol catalyst, a solution of 0.3 mmol styrene in 1:1 dichloromethane: methanol (2 mL) was added at 2–4 °C under argon. In the case of the manganese catalysts, 0.3 mmol 1-methylimidazole was also added. After 10 min stirring, 0.5 mmol UHP was added in three portions at a reaction temperature of 4 °C. The reaction mixture was stirred for 8 h at room temperature. The progress of the reaction was monitored by periodic sampling for GC determination. Chlorobenzene was used as standard for quantitative determination of product.

Conclusion

In summary, while conversions using UHP and H_2O_2 as primary oxidant were similar, in the case of UHP, the selectivity for styrene epoxide production was better. So, UHP as a water-free oxidant could be used as a stable, cheap, and environmentally friendly oxidant, capable of use in organic solvents and for water sensitive materials.

The efficiency of these catalysts was strongly dependent on the structure of the dibasic Schiff base ligands. When 5,5′-dinitro-N,N′—bis(salicylidene)pyridinediamine ligand $\mathbf{L^3}$ was coordinated with manganese, the resulting complex catalysts **3** gave epoxide yields of 70% within 8 h, notably lower than the 93% obtained with catalyst **2** and lower than the 89% obtained with **1**. This could be due to the strong electron withdrawing effect of the nitro group of complex **3.** The vanadium(IV) catalysts **4**–**6** exhibit obviously different activities, as shown in Table 4. It is evident that the vanadyl catalysts **4**–**6** are less active for the epoxidation of styrene than the Mn catalysts **1**–**3**. Similar selectivities could be reached at about 8 h for both catalysts; however, the highest conversion and selectivity for catalyst **5** were only 34 and 75%, respectively, but those for catalyst **2** were 48 and 93%, respectively. These results could be due to several factors, such as the nature of the metals, their ability to coordinate the reactants, the solubility of the complexes, etc.

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