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Synthesis and characterization of mono- and bi-metallic Mn(III) complexes containing salen type ligands

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A mononuclear complex **1**, of Mn(III) with a Schiff-base ligand L [L = *N*,*N*′-ethylenebis(3-formyl-5-methylsalicylaldimine)] has been synthesized and structurally characterized. A series of binuclear complexes, $MnML'Cl_xsolv_y$ [M = Zn(II), Cu(II), Ni(II), Co(II), Fe(III), and Mn(III); x = 3 or 4 depending on the oxidation state of M; L′ is the aniline condensation product of L; y = 1, 2 or 3 and solv = H_2O or CH_3OH] have been prepared by the reaction of **1**, aniline and M(II/III) chloride with a 1 : 3 : 1.2 molar ratio in methanolic media. These bimetallic complexes were characterized by elemental analyses, UV-Vis and IR spectroscopies, magnetic susceptibilities and thermogravimetric analyses. The results of magnetic susceptibility measurements at 300 K indicate that all the metal ions are in their high spin states. The catalytic properties of these complexes for epoxidation of alkenes have been investigated using PhIO as a terminal oxidant. The binuclear Mn(III) complexes are less efficient epoxidation catalysts than the mononuclear Mn(III) complex, **1**. The reduced activities of the bimetallic complexes may be due to both the low rates of formation of a Mn(V)=O intermediate and the transfer of oxygen from this intermediate to the alkene. Furthermore, the bimetallic complexes also transformed into a catalytically inactive species in the presence of PhIO as indicated by UV-Vis spectroscopic studies.

Introduction

Mn(III) complexes of salen type ligands have attracted much interest in the last few decades because of their unique catalytic activity, especially as epoxidation catalysts, in the presence of a terminal oxidant like iodosylbenzene.[1–19] Numerous salen ligands have been prepared to investigate steric, electronic and overall structural effects on the catalytic activity of the Mn(III) center. *N*,*N*′-Ethylenebis(3-formyl-5-methylsalicylaldimine) (L) is an extensively studied salen type ligand. Surprisingly, to the best of our knowledge, its Mn(III) complex has not yet been reported. Moreover, no mononuclear complex of the ligand has been structurally characterized by X-ray crystallography in order to delineate the donor atoms of the ligand. This ligand may be used to synthesize binuclear complexes with a second metal ion in close proximity to the Mn(III) center and thereby provide a means of studying the effect of a second metal on the catalytic activity of Mn(III). Further understanding of metal–metal interactions is very important because the interactions are critical in some bimetallic metalloproteins. Some illustrative examples of bimetallic metalloproteins involved in the reaction and transport of dioxygen in biological systems[20–23] are given below. In cytochrome c oxidase, the binding and initial reduction of dioxygen occurs on a site of coupled copper and iron centers. The transport of oxygen requires a bicopper center in hemocyanin and a biferrous center in hemerythrin. Here, we report the syntheses of bimetallic Mn(III) complexes based on the monomanganese complex of L. The catalytic activities of these complexes for the epoxidation of alkenes were investigated to probe the influence of the second metal on the catalytic efficiency of the Mn(III) center.

Results and discussion

Synthesis and characterization

In 1972, Okawa snd Kida[24] first reported Ni(II) and Cu(II) complexes of L (L = *N*,*N*′-ethylenebis(3-formyl-5-methylsalicylaldimine) and in 1981 Gagne *et al.*[25] synthesized Ni(II) and Cu(II) complexes of a similar ligand system. Those complexes were characterized by elemental analyses, magnetic moment, IR and UV-Vis spectroscopic studies. The authors presumed that the metal ions bind preferentially to the N_2O_2 site. To date no mononuclear metal complex of ligand L has yet been characterized by X-ray crystallography. Therefore, we prepared Mn(III)LCl, **1** and characterized it structurally by the single crystal X-ray diffraction method (*vide infra*).

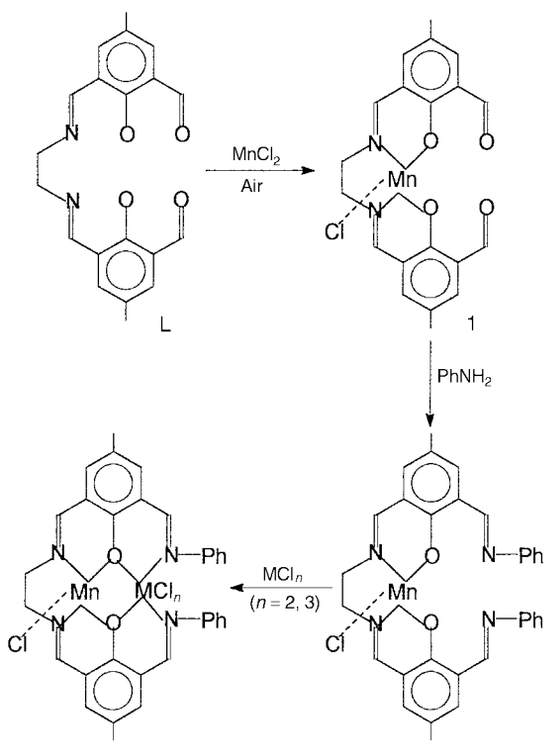
Bimetallic complexes containing Mn(III) could not be successfully prepared from Mn(III)LCl. This difficulty was overcome by condensing the formyl groups with aniline to create another coordination site for the second metal in Mn(III)L′Cl (Scheme 1).[25] The six bimetallic complexes $MMnL'Cl_xsolv_y$ (for solv = CH_3OH: M = Zn(II), x = 3, y = 2, **2**; for solv = H_2O: M = Cu(II), $x = y$ = 3, **3**; M = Ni(II), $x = y$ = 3, **4**; M = Co(II), x = 3, y = 1, **5**; M = Fe(III), x = 4, y = 1, **6**; M = Mn(III), x = 4, y = 1, **7**) were prepared by the reactions of Mn(III)L′Cl with various metal chlorides. We tried but failed to prepare Pd(II)-Mn(III)$L'Cl_xsolv_y$ by the same procedure. This failure may be ascribed to the size of the second N_2O_2 site which is too small to accommodate the second row transition metal ion.

The mononuclear Mn(III) complex **1** exhibits characteristic IR bands at 1660, 1625 and 1546 cm^{-1} assigned to C=O, C=N and skeletal vibrations.[24,25] The 1660 cm^{-1} band is absent in the spectra of all the binuclear complexes whereas the other two bands remain, suggesting the complete condensation of the formyl groups of L with aniline. The effective magnetic moments at 300 K and the expected spin-only values are collected in Table 1. The spin-only values in Table 1 were calculated using the equations $\mu_{Mn} = 2[S_{Mn}(S_{Mn} + 1)]^{\frac{1}{2}}$ for complex **1** and $\mu_{Mn\text{-}M} = (\mu_{Mn}^2 + \mu_M^2)^{\frac{1}{2}}$ for binuclear complexes. The effective magnetic moment of complex **1** agrees well with that predicted for a high-spin d^4 configuration Mn(III) ion in the complex. The effective magnetic moments of the binuclear complexes are in good agreement with their corresponding spin-only value assuming no magnetic interaction between the metal ions.

Table 1 Effective magnetic moments of the complexes **1**–**7** at 300 K

Complex	μ_{eff}/μ_B	$\mu_{spin\ only}{}^a/\mu_B$	M: S^b
1	4.79	4.90	—
2	4.78	4.90	Zn(II): 0
3	5.09	5.20	Cu(II): 1/2
4	5.61	5.66	Ni(II): 1
5	6.16	6.24	Co(II): 3/2
6	7.48	7.68	Fe(III): 5/2
7	6.78	6.93	Mn(III): 2

[a] Calculated based on the assumption that Mn(III) is in a high spin state in all the complexes. [b] The metal ion and the spin state of the second metal in complexes **2**–**7** used to calculate $\mu_{spin\ only}$.



Scheme 1

Therefore, these data indicate that both Mn(III) and the second metal ion are in their high-spin states. Complexes **1**, **2** and **7** are EPR silent and thereby exclude the presence of Mn(II) impurities in these complexes. The coordinating solvents have been verified by the appropriate weight losses in their thermogravimetric (TG) analyses. These weight losses and their corresponding temperatures are indicated in the Experimental section.

Structure of complex 1

The structure of this complex is shown in Fig. 1; selected bond distances and angles are given in Table 2. Mn(III) in the complex is penta coordinated and the geometry can be best described as square pyramidal (Fig. 1). It also contains 0.39 mol of water of crystallization which is different from that found for the sample described in the Experimental section. This results from different crystallization conditions. The two phenolic O atoms and two imine N atoms of the Schiff base occupy the basal plane of the square pyramid. This indicates clearly that the formyl groups in this ligand do not coordinate to Mn(III). The structure of this N_2O_2 coordination site also supports the proposed structures of CuL and NiL.[24,25] The Mn–O distances of 1.878(3) Å (for both) and Mn–N distances of 1.969(3) and 1.987(3) Å (Table 2) are comparable to those previously reported for Mn(III)(salen) derivatives in which there are no

Table 2 Selected bond distances (Å) and bond angles (°) for complex **1**·0.39H_2O, Mn(III)LCl·0.39H_2O [L = *N*,*N*′-ethylenebis(3-formyl-5-methylsalicylaldiimine)]

Mn(1)–O(1)	1.878(3)	Mn(1)–O(2)	1.878(3)
Mn(1)–N(1)	1.987(3)	Mn(1)–N(2)	1.969(3)
Mn(1)–Cl(1)	2.3691(14)	O(1)–C(1)	1.341(5)
O(2)–C(16)	1.318(5)	N(1)–C(7)	1.284(5)
N(2)–C(10)	1.291(5)	N(1)–C(8)	1.481(5)
N(2)–N(9)	1.472(5)	C(8)–C(9)	1.513(7)
C(6)–C(7)	1.437(6)	C(1)–C(6)	1.395(6)
C(10)–C(11)	1.437(6)	C(11)–C(16)	1.411(6)
O(1)–Mn(1)–N(1)	89.65(13)	O(2)–Mn(1)–N(2)	91.26(14)
O(1)–Mn(1)–O(2)	91.47(13)	N(1)–Mn(1)–N(2)	81.92(14)
O(1)–Mn(1)–Cl(1)	99.81(11)	O(2)–Mn(1)–Cl(1)	101.84(11)
N(1)–Mn(1)–Cl(1)	95.96(11)	N(2)–Mn(1)–Cl(1)	98.32(11)
O(1)–Mn(1)–N(2)	160.70(15)	O(2)–Mn(1)–N(1)	161.70(15)

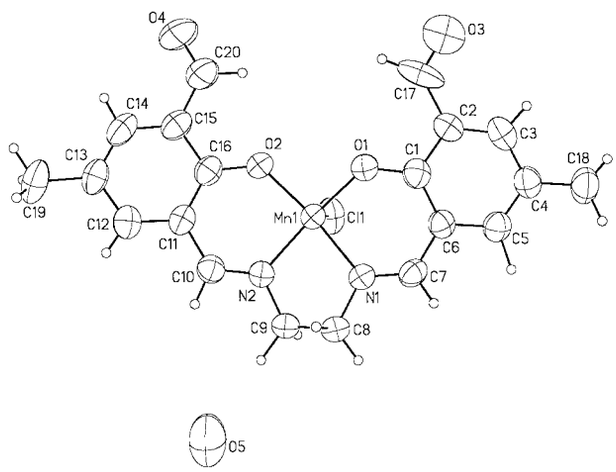


Fig. 1 ORTEP[35] drawing of complex **1**·0.39H_2O with the atom numbering scheme. Thermal ellipsoids are scaled to enclose 50% electron density. Hydrogens have an arbitrary radius of 0.1 Å.

formyl groups in the salen ligand.[1–3,26,27] The four atoms in the basal plane deviate slightly from planarity. The average deviation from the best plane through these four atoms is 0.0042 Å, with O(1) and N(2) sitting above the plane while O(2) and N(1) sit below it. Mn(III) lies 0.3035 Å above the basal plan. A comparison among analogous penta coordinated Schiff-base complexes of Mn(III), [Mn(salen)Cl],[26] [Mn(acen)Cl] [H_2acen = *N*,*N*′-ethylenebis(acetylacetone imine)][27] and [Mn(tetramethylsalen)Cl][3] shows that these complexes all have similar structures but in [Mn(salen)Cl] the Mn atom is only 0.19 Å above the N_2O_2 plane, whereas in **1**, [Mn(acen)Cl] and in [Mn(tetramethylsalen)Cl] complexes the corresponding distances are 0.3035, 0.344 and 0.305 Å, respectively. This distinction is well correlated with their respective Mn–Cl bond lengths. The Mn–Cl distances are 2.3691(14), 2.381(1) and 2.391(2) Å in **1**, (acen) and (tetramethylsalen) complexes, respectively, whereas this distance in the (salen) complex is noticeably longer, 2.461(1) Å.

Epoxidation of alkenes

The catalytic activities of the monomanganese complex **1** and the bimetallic complexes **2**–**7** were compared for the epoxidation of alkenes by a terminal oxidant. The epoxidations were carried out in CH_3CN using PhIO as the terminal oxidant at 25 °C. The amounts of PhI and epoxide formed on epoxidation of (*E*)-stilbene catalyzed by complexes **1**–**7** as a function of time are shown in Fig. 2 and 3. Within 5 min, 0.160 mmol of PhI and 0.117 mmol of *trans*-stilbene oxide were formed on epoxidation of (*E*)-stilbene by complex **1**, whereas, those amounts were 0.120 to 0.020 mmol and 0.082 to 0.0025 mmol, respectively, when the binuclear complexes **2**–**7** were used as catalysts. In all cases, the initial rates of formation of PhI and

Table 3 Yields of epoxides from the reactions of alkenes with PhIO catalyzed by complexes **1**–**7**[a]

Olefins	Yield of epoxides with different catalysts[b] (%)						
	1	**2**	**3**	**4**	**5**	**6**	**7**
(*E*)-PhCH=CH–Ph	86	63	25	63.5	73	45	82
(*Z*)-PhCH=CH–Ph	48 (*cis*)	22	11	15	21	19	31
	25 (*trans*)	12	5	8	10	9	17
$PhCH=CH_2$	63	38	12	37	47	28	51
(*E*)-PhCH=CH–CH_3	53	21	[c]	21	39	19	43
(*Z*)-PhCH=CH–CH_3	28	8	[c]	6	11	[c]	14
	15 (*trans*)	[c]	[c]	[c]	6	[c]	9

[a] 0.300 mmol of alkene, 1.00×10^{-2} mmol of catalyst and 0.300 mmol of PhIO in 5 mL acetonitrile at 25 °C. [b] Yields are based on iodobenzene formed, determined by GC analysis. The products for (*E*)-alkenes are *trans*-epoxides only. [c] Yield is negligibly low.

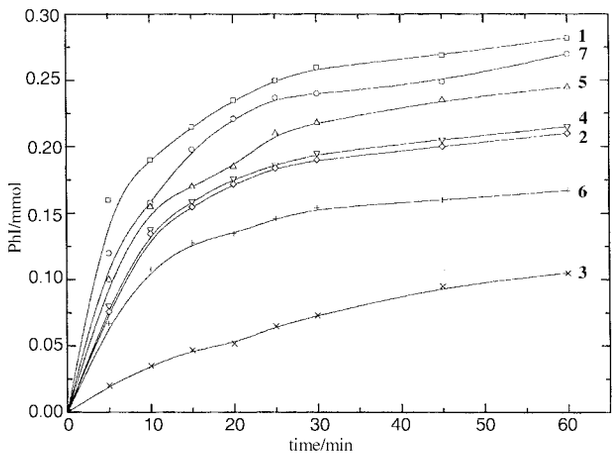


Fig. 2 PhI formation as a function of time in the epoxidation of (*E*)-stilbene with PhIO catalyzed by complexes **1**–**7** (0.300 mmol of alkene, 1.00×10^{-2} mmol of catalyst and 0.300 mmol of PhIO in acetonitrile (5 mL) at 25 °C).

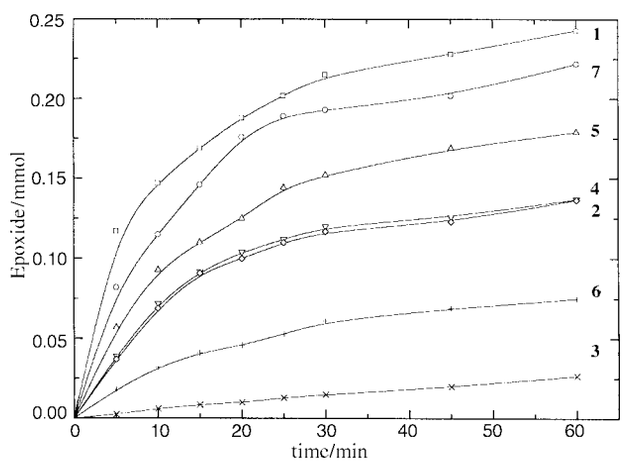


Fig. 3 Epoxide formation as a function of time for the epoxidation of (*E*)-stilbene with PhIO catalyzed by complexes **1**–**7** (0.300 mmol of alkene, 1.00×10^{-2} mmol of catalyst and 0.300 mmol of PhIO in acetonitrile (5 mL) at 25 °C).

epoxide were rapid, except for the reaction catalyzed by complex **3**. After 30 min the rates of formation of PhI and epoxide formation slowed down in every case. From Fig. 2 and 3, the effectiveness of the catalysts in producing *trans*-stilbene oxide followed the order **1** > **7** > **5** > **4** ≈ **2** > **6** > **3**. The percentages of epoxide (with respect to PhI) formed after a one hour reaction period by complexes **1**–**7** are collected in Table 3. We also studied the epoxidation of (*Z*)-stilbene, styrene, (*E*)-β-methylstyrene and (*Z*)-β-methylstyrene under the same conditions. From the results given in Table 3, it is clear that the order of catalytic activity of the metal complexes is independent of the nature of alkene. The reactivities of the alkenes follow the order: (*E*)-stilbene > (*Z*)-stilbene > styrene > (*E*)-β-methylstyrene > (*Z*)-β-methylstyrene. It is noteworthy that *trans*-alkenes produce *trans*-epoxides, whereas *cis*-disubstituted alkenes produce both *cis*- and *trans*-epoxides on epoxidation.

The experimental results indicated that the presence of a second metal in complexes **2**–**7** reduces the catalytic activity of the Mn(III) centers. In order to further understand the interaction of the catalyst with PhIO, we studied the reactions of the catalysts **1**–**7** with PhIO (0.010 mmol catalyst and 0.300 mmol PhIO in 5 mL CH_3CN) in the absence of any substrate. The Mn(III) complexes react with PhIO to produce iodoxybenzene $PhIO_2$.[28] Complex **1** produced 0.130 mmol of PhI and the binuclear complexes yielded PhI in the range of 0.060 to 0.090 mmol after 1 h of reaction. These data, which are consistent with the slow rates of formation of PhI for complexes **2**–**7** shown in Fig. 2, reveal that the low efficiency of the binuclear complexes for alkene epoxidation compared to that of the corresponding mononuclear Mn(III) is not due to the decomposition of PhIO by any other path. If a Mn(V)=O intermediate, which was first proposed by Kochi *et al.*[1] and later supported by the electrospray tandem mass spectroscopic data,[29] is formed in both the decomposition of PhIO and the epoxidation reaction, then this intermediate is more slowly formed for the binuclear complexes **2**–**7** than for **1**. Since the yields of epoxide relative to PhI are low for the complexes **2**–**7** catalyzed reactions, the effectiveness of the transfer of an oxygen atom from the Mn(V)=O intermediate to the alkene is also reduced for these complexes. One reasonable explanation is that the presence of the second metal may destabilize the Mn(V)=O intermediate because of a repulsive charge interaction between Mn(V) and the second metal as well as a possible charge-induced bonding change. However, since the order of effectiveness of catalysts **2**–**7** does not correlate with the charge of the second metal ion, there must be other factors which influence the activity of the bimetallic complexes. The affinity of the second metal for alkenes is not well recognized. So the coordination of alkenes to the second metal may not be a significant factor. The presence of the second metal may also affect the coordination environments of the reactive Mn(III) center or Mn(V)=O intermediate. Unfortunately, up to now, we failed to obtain single crystals of any binuclear complex. On the other hand, crystal structures of Mn(III) complexes of salen derivatives indicate that salen derivatives are pliable in forming the manganese complexes.[30] Therefore, a change in the coordination environments for Mn(III) induced by the second metal may play an important role in the catalytic activity of complexes **1**–**7**.

To examine the nature of the complexes **1**–**7** in the catalytic process, we studied the UV-Vis spectral changes for complexes **1**–**7** in the presence of PhIO (1.00×10^{-3} mmol complex in acetonitrile (5 mL) was treated with 0.300 mmol PhIO). The results for complexes **1** and **5** are shown in Fig. 4A and 4B, respectively. Complex **5** was chosen as a representative example

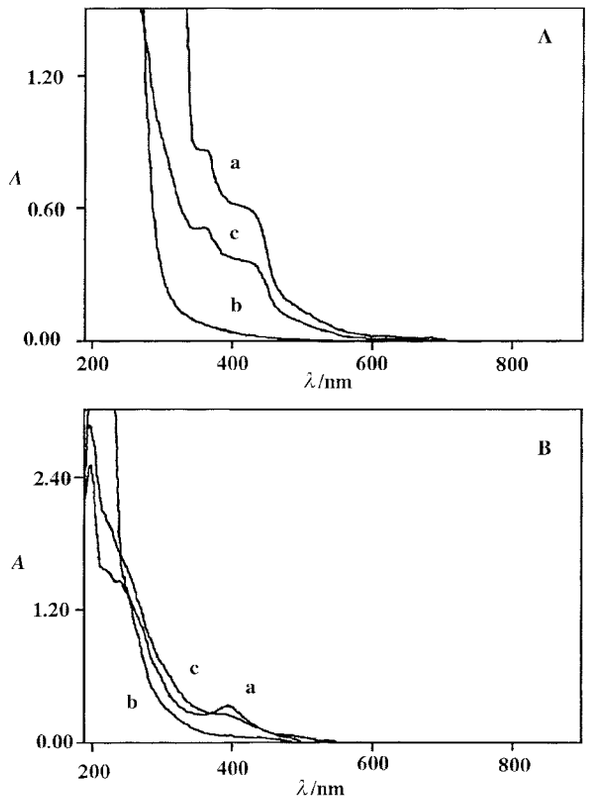


Fig. 4 UV-Vis spectral pattern of complex **1** (A) and **5** (B): (a) 2.00×10^{-3} M solution of complex in acetonitrile at room temperature; (b) one hour after addition of PhIO (0.300 mmol) (sample diluted by ≈2-fold) and (c) after one day of the reaction (sample diluted by ≈2-fold).

of the binuclear complexes as they all exhibited similar changes in their UV-Vis spectra. Fig. 4 shows spectra before addition of PhIO (a); after 1 h of reaction (b) and after one day of reaction (c). PhIO was completely reacted after one day in a solution of complex **1** while a substantial amount of PhIO remained unreacted in the solutions of complexes **2**–**7**. Complex **1** and the binuclear complexes exhibited similar spectra after 1 h reaction (spectra (b); Fig. 4). After one day, complex **1** produced spectrum (c) which is identical to its original one (spectrum (a), Fig. 4A) except for the contribution from PhI, whereas, binuclear complexes yielded spectrum (c) (Fig. 4B) which was somewhat different from their original spectra (the spectrum was measured after removing the unreacted PhIO from the reaction mixture).

The species **1c** and **5c** which were responsible for spectra (c) in Fig. 4A and 4B, respectively and were obtained after one day reaction of **1** and **5** with PhIO, were further treated with fresh PhIO (0.300 mmol). GC analyses were performed on the reaction mixtures after 1 h of reaction. **5c** was observed to be inactive to produce PhI, whereas, **1c** was found to be as reactive as **1** and this reactivity was noticed to be retained beyond ten cycles. Furthermore **1c** is as effective as **1** in catalyzing the epoxidation reaction while **5c** is not an active catalyst. From these observations, we may infer that initially complex **1** as well as the binuclear complexes react with PhIO in a similar fashion but at reduced rates for the binuclear complexes. However, the binuclear complexes lose their reactivity gradually due to their conversion to some inactive species, whereas, complex **1** retains its reactivity for a long time and consequently exhibits a higher efficiency.

In addition to the oxidation of alkenes of styrene derivatives, we also studied the catalytic oxidation of simple alkenes like cyclohexene with complexes **1**–**7**. Very low percentage yields of cyclohexene epoxide (15%) and cyclohexanol (5%) were observed when complex **1** was used as a catalyst, whereas, no oxidation product was detected for the binuclear catalysts. The poor efficiency of complex **1** is proposed to be related to its penta coordinate geometry as reported earlier.[3,31] We also performed the oxidation of cyclohexane using complexes **1**–**7** as catalyst. No oxidation product was detected even with complex **1**. This indicates that the Mn(v)=O species generated from complexes **1**–**7** are not as reactive as that which was obtained from Kochi's 5,5′-dinitrosalen Mn(iii) complex to activate the C–H bonds of alkanes.[1]

Conclusion

A series of bimetallic Mn(iii) complexes $MMnL'Cl_xsolv_y$ (for solv = CH_3OH: M = Zn(ii), $x = 3$, $y = 2$, **2**; for solv = H_2O: M = Cu(ii), $x = y = 3$, **3**; M = Ni(ii), $x = y = 3$, **4**; M = Co(ii), $x = 3$, $y = 1$, **5**; M = Fe(iii), $x = 4$, $y = 1$, **6**; M = Mn(iii), $x = 4$, $y = 1$, **7**), were synthesized from the monomanganese complex Mn(iii)LCl, **1**. The X-ray structure of **1** indicates that the coordination site is N_2O_2, confirming the earlier assumptions of the coordination site of L. The presence of the second metal ion does not alter the high spin state of the Mn(iii) ions in the bimetallic complexes **2**–**7**. In the epoxidation of alkenes, including (*E*)-stilbene, (*Z*)-stilbene, styrene, (*E*)-β-methylstyrene and (*Z*)-β-methylstyrene, by PhIO, **1**–**7** yielded essentially the same products, *i.e.*, *trans*-alkene to *trans*-epoxide and *cis*-alkene to a mixture of *trans*- and *cis*-epoxides. From the rate of formation of PhI from PhIO and epoxide from (*E*)-stilbene, it is obvious that the second metal ion in **2**–**7** slows down the formation of the active intermediate Mn(v)=O and reduces the efficiency of the transfer of an oxygen atom to the alkene. The influence of the second metal follows the order Cu(ii) > Fe(iii) > Zn(ii) ≈ Ni(ii) > Co(ii) > Mn(iii). Furthermore, in the presence of PhIO, the bimetallic complexes also transform into inactive species in contrast to the monometallic complex **1**, which is stable and reduced PhIO to PhI effectively. Therefore, the second metal exhibits a negative effect on the catalytic activity of Mn(iii) in catalyzing the epoxidation of alkenes by PhIO.

Experimental

Physical measurements

Elemental analyses (C, H, and N) of the complexes were carried out on a Heraeus CHN rapid analyzer. The metal contents of the complexes were determined by a Perkin-Elmer ICP mass spectrometer (model Optima 3000 DV). NMR spectra were recorded on a Bruker AC300 spectrometer, IR spectra (as KBr discs) were recorded on a Jasco FT-IR (model 300E) spectrophotometer and electronic spectra (in dry methanol) were recorded on a Perkin-Elmer Lambda 5 UV-Vis spectrophotometer. Magnetic susceptibilities were measured on a Quantum Design MPMS SQUID magnetometer (applied field 5 T) at 300 K. Diamagnetic corrections were applied using Pascal's constants.[32] GC analysis was performed on a Shimadzu Gas Chromatograph 8A instrument equipped with a flame ionization detector. Thermogravimetric analysis was carried out with a Seiko 300 Thermal Analyzer under a nitrogen atmosphere.

Synthesis

2,6-Diformyl-4-methylphenol[25] and *N*,*N*′-ethylenebis(3-formyl-5-methylsalicylaldimine)[24] (L) were prepared according to the literature methods. Alkenes were purchased from Aldrich and used without further purification. The epoxides were obtained either from Aldrich or prepared by the epoxidation of the corresponding alkene with *m*-chloroperbenzoic acid (Aldrich) in methylene chloride.[33] Other chemicals and solvents were reagent grade, and were used without further purification. Solvents were dried according to standard procedures and distilled before use.

MnLCl·2H$_2$O (1·2H$_2$O). To a heated suspension of L (7.04 g, 0.02 mol) in ethanol (50 mL), an aqueous solution (20 mL) of MnCl$_2$·4H$_2$O (3.96 g, 0.02 mol) was added dropwise. A brown color developed immediately upon dissolution of the ligand. The resulting solution was allowed to stir open to the atmosphere for 12 h. A brown complex precipitated and was isolated by filtration, washed with water and dried in vacuum at 50 °C for 12 h. Yield 8.5 g (89% with respect to L). The complex thus obtained was recrystallized from acetonitrile (Found: C, 50.36; H, 5.05; N, 5.96; Mn, 11.38. $C_{20}H_{18}N_2O_4MnCl·2H_2O$ requires C, 50.37; H, 4.62; N, 5.88; Mn, 11.53%). IR(KBr)/cm^{-1}: 1660 (C=O), 1625 (C=N) and 1546 (skeletal vibration). UV-Vis-(MeOH)/nm: 421 (sh, $\varepsilon = 9500$), 361 ($\varepsilon = 12000$). TG analysis: 0.356 mg weight loss (7.56% of 4.71 mg complex; expected weight loss: 7.56%) at 123 °C.

MnZnL′Cl$_3$·CH$_3$OH (2). Aniline (0.41 mL; 4.50 mmol) in dry methanol (10 mL) was added dropwise to a methanolic (15 mL) solution of MnLCl·2H$_2$O (0.715 g, 1.50 mmol) with constant stirring at room temperature. After 1 h solid ZnCl$_2$ (0.245 g, 1.80 mmol) was added to that solution and the stirring was continued for an additional 1 h. The mixture was then cooled in an ice bath for 40 min. The yellowish brown product was isolated by filtration, washed with dry methanol rapidly to remove the unreacted complex **1**·2H$_2$O which is highly soluble in methanol and dried under vacuum. Yield: 0.87 g (76%). Recrystallization was accomplished by dissolving the complex in a minimum amount (5 mL) of dry methanol followed by dropwise addition of dry ether (10 mL) (Found: C, 52.42; H, 4.36; N, 7.30; Mn, 7.19; Zn, 8.83. $C_{32}H_{28}N_4O_2Cl_3$-MnZn·CH$_3$OH requires C, 52.18; H, 4.22; N, 7.38; Mn, 7.24; Zn, 8.62%). IR (KBr)/cm^{-1}: 1637 (C=N) and 1542 (skeletal vibration). UV-Vis(MeOH)/nm: 428 (sh, $\varepsilon = 9000$), 366 ($\varepsilon =$ 14000). TG analysis: 0.20 mg weight loss (4.27% of 4.68 mg sample; expected weight loss: 4.22%) at 112 °C.

MnCuL′Cl$_3$·3H$_2$O (3). To a methanolic solution (15 mL) of MnLCl·2H$_2$O (0.715 g, 1.50 mmol), aniline (0.41 mL, 4.50 mmol) in methanol (10 mL) was added dropwise. The resulting solution was refluxed for 2 h under a nitrogen atmosphere and solid CuCl$_2$·2H$_2$O (0.308 g, 1.80 mmol) was added to it. The mixture was further refluxed for 2 h. Solvent was removed partially on a rotary evaporator and the product was isolated by filtration, washed with methanol and dried under vacuum. Yield: 0.91 g (78%). This crude product was recrystallized twice from methanol solution by addition of ether (Found: C, 49.14; H, 4.33; N, 7.16; Mn, 6.83; Cu, 8.05. $C_{32}H_{28}N_4O_2Cl_3MnCu$·3H$_2$O requires C, 49.29; H, 4.36; N, 7.18; Mn, 7.05; Cu, 8.16%). IR(KBr)/cm^{-1}: 1637 (C=N) and 1542 (skeletal vibration). UV-Vis(MeOH)/nm: 440 (sh, $\varepsilon = 6000$), 371 ($\varepsilon = 18000$). TG analysis: 0.31 mg weight loss (7.06% of 4.39 mg sample; expected weight loss: 6.93%) at 130 °C.

The remaining binuclear complexes were prepared by the same procedure as that for MnCuL′Cl$_3$·3H$_2$O **(3)**. The analytical data are given below.

MnNiL′Cl$_3$·3H$_2$O (4). Yield: 79% (Found: C, 49.72; H, 4.43; N, 7.22; Mn, 6.86; Ni, 7.50. $C_{32}H_{28}N_4O_2Cl_3MnNi$·3H$_2$O requires C, 49.60; H, 4.39; N, 7.23; Mn, 7.09; Ni, 7.58%). IR(KBr)/cm^{-1}: 1631 (C=N) and 1543 (skeletal vibration). UV-Vis(MeOH)/nm: 390 (sh, $\varepsilon = 1400$), 368 ($\varepsilon = 19000$). TG analysis: 0.36 mg weight loss (7.07% of 5.09 mg sample; expected weight loss: 6.97%) at 127 °C.

MnCoL′Cl$_3$·H$_2$O (5). Yield: 73% (Found: C, 51.92; H, 4.11; N, 7.62; Mn, 7.36; Co, 7.81. $C_{32}H_{28}N_4O_2Cl_3MnCo$·H$_2$O requires C, 52.00; H, 4.06; N, 7.58; Mn, 7.44; Co, 7.98%). IR(KBr)/cm^{-1}: 1627 (C=N) and 1554 (skeletal vibration). UV-Vis(MeOH)/nm: 395 (sh, $\varepsilon = 11000$), 370 ($\varepsilon = 20000$). TG analysis: 0.19 mg weight loss (2.63% of 7.21 mg complex; expected weight loss: 2.44%) at 118 °C.

MnFeL′Cl$_4$·H$_2$O (6). Yield: 68% (Found: C, 49.74; H, 3.95; N, 7.21; Mn, 7.03; Fe, 7.50) $C_{32}H_{28}N_4O_2Cl_4MnFe$·H$_2$O requires C, 49.82; H, 3.89; N, 7.27; Mn, 7.13; Fe, 7.62%). IR(KBr)/cm^{-1}: 1638 (C=N) and 1548 (skeletal vibration). UV-Vis(MeOH)/nm: 499 (sh, $\varepsilon = 7500$), 359 ($\varepsilon = 15000$). TG analysis: 0.21 mg weight loss (2.74% of 7.29 mg complex; expected weight loss: 2.33%) at 122 °C.

Mn$_2$L′Cl$_4$·H$_2$O (7). In this case the reflux was carried out in open atmosphere. Yield: 76% (Found: C, 49.78; H, 3.73; N, 7.22; Mn, 14.02. $C_{32}H_{28}N_4O_2Cl_4Mn_2$·H$_2$O requires C, 49.88; H, 3.89; N, 7.27; Mn, 14.27%). IR(KBr)/cm^{-1}: 1629 (C=N) and 1550 (skeletal vibration). UV-Vis(MeOH)/nm: 428 (sh, $\varepsilon = 11000$), 372 ($\varepsilon = 16000$). TG analysis: 0.15 mg weight loss (2.41% of 7.48 mg sample; expected weight loss: 2.33%) at 115 °C.

Iodosylbenzene. This was prepared by hydrolysis of the corresponding diacetate with aqueous sodium hydroxide as reported in the literature.[34] Freshly prepared PhIO was used in every epoxidation experiment.

Epoxidation of alkenes catalyzed by complexes 1–7

All epoxidation reactions were carried out by the same procedure. In a typical experiment, 0.300 mmol of alkene and 1.00×10^{-2} mmol of catalyst were treated with acetonitrile (5 mL) under a nitrogen atmosphere. Chlorobenzene (0.300 mmol) was added as an internal standard for GC analysis. A GC analysis was performed by withdrawing aliquots in small portions from the reaction mixture to establish the initial conditions. Afterwards 0.066 g (0.300 mmol) of PhIO was added to the solution under a nitrogen flow. The reaction mixture was then sampled periodically by withdrawing aliquots in small portions for GC analysis. Quantification of the product was done by the internal standard method.

The product of epoxidation was identified by ^{1}H NMR spectroscopy. Typically, the sample was prepared by the following procedure.[1] Iodosylbenzene (0.066 g, 0.300 mmol) was added to a solution containing 0.054 g (0.300 mmol) of (*E*)- or (*Z*)-stilbene and 1.00×10^{-2} mmol of catalyst in dry acetonitrile (5 mL) under a nitrogen atmosphere. The suspension was stirred vigorously for 1 h. Then the solvent was removed under reduced pressure. Anhydrous ether (5 mL) was added to the brown residue and the ether solution was carefully filtered through a cannula. Then, ether was removed under reduced pressure (alternatively, the ether solution was chromatographed on a silica gel using hexane and ether as an eluent). The residue was dissolved in 0.4 mL $CDCl_3$ and a ^{1}H NMR spectrum was measured. The singlet peaks at δ 4.35 and 3.85 are characteristic of the proton resonances of (*Z*)- and (*E*)-stilbene oxide respectively.

X-Ray crystallography

Single crystals of complex **1**·0.39H$_2$O suitable for X-ray diffraction were grown by slow diffusion of anhydrous ether into an acetonitrile–acetone (1 : 1 v/v) mixed solution of **1** at room temperature. Crystal data are summarized in Table 4. Intensity data were collected at 293 K on a Siemens Smart CCD diffractometer using monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) from a graphite single crystal. A total of 14554 reflections were collected with 5553 independent reflections ($R_{int} = 4.5\%$). The intensities were corrected for Lorentz-polarization effects and absorption using the SHELXTL-PC[36] package ($T_{min,\ max} = 0.8296, 0.9630$). The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares. All hydrogen atoms were

Table 4 Crystallographic data for complex **1**·0.39H_2O, Mn(III)LCl·0.3H_2O [L = *N*,*N*′-ethylenebis(3-formyl-5-methylsalicylaldiimine)]

Empirical formula	$C_{20}H_{18.78}ClMnN_2O_{4.39}$
Formula weight	447.87
Space group	*C*2/*c*
a/Å	26.0049(2)
b/Å	14.6410(9)
c/Å	13.6091(9)
β/°	117.987(2)
V/Å^3	4575.4(5)
Z	8
D_c/Mg m^{-3}	1.300
μ_{cal}/mm^{-1}	0.0721
θ/°	1.65 to 28.32
Final R^a indices [$I > 2\sigma(I)$]	$R(F) = 0.0622$, $R_w(F^2) = 0.2032$
Final *R* indices [all reflections]	$R(F) = 0.1201$, $R_w(F^2) = 0.2342$

^{a} $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_c|$; $R_w(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

placed in ideal positions according to the riding model with isotropic *U* values in structure factor calculations. All calculations were performed on a Micro VAX III computer with the Siemens SHELXTL PLUS (VMS)[37] program.

CCDC reference number 186/1835.

See http://www.rsc.org/suppdata/dt/a9/a908304i/ for crystallographic files in .cif format.

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