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Dinuclear Mn(II,II) complexes: magnetic properties and microwave assisted oxidation of alcohols†

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A series of six new mixed-ligand dinuclear Mn(II,II) complexes of three different hydrazone Schiff bases (H_3L^1, H_3L^2 and H_3L^3), derived from condensation of the aromatic acid hydrazides benzohydrazide, 2-aminobenzohydrazide or 2-hydroxybenzohydrazide, with 2,3-dihydroxy benzaldehyde, respectively, is reported. Reactions of $Mn(NO_3)_2{\cdot}4H_2O$ with the H_3L^{1-3} compounds, in the presence of pyridine (1 : 1 : 1 mole ratio), in methanol at room temperature, yield $[Mn(H_2L^1)(py)(H_2O)]_2(NO_3)_2{\cdot}2H_2O$ (**1**·2H_2O), $[Mn(H_2L^2)(py)(CH_3OH)]_2(NO_3)_2{\cdot}4H_2O$ (**2**·4H_2O) and $[Mn(H_2L^3)(py)(H_2O)]_2(NO_3)_2$ (**3**) respectively, whereas the use of excess pyridine yields complexes with two axially coordinated pyridine molecules at each Mn(II) centre, *viz.* $[Mn(H_2L^1)(py)_2]_2(NO_3)_2{\cdot}H_2O$ (**4**·H_2O), $[Mn(H_2L^2)(py)_2]_2(NO_3)_2{\cdot}2H_2O$ (**5**·2H_2O) and $[Mn(H_2L^3)(py)_2]_2(NO_3)_2{\cdot}2CH_3OH$ (**6**·2CH_3OH), respectively. In all the complexes, the $(H_2L^{1-3})^-$ ligand coordinates in the keto form. Complexes **1**·2H_2O, **2**·4H_2O, **4**·H_2O, **5**·2H_2O and **6**·2CH_3OH are characterized by single crystal X-ray diffraction analysis. The complexes **1**, **2** and **6**, having different coordination environments, have been selected for variable temperature magnetic susceptibility measurements to examine the nature of magnetic interaction between magnetically coupled Mn(II) centres and also for exploration of the catalytic activity towards microwave assisted oxidation of alcohols. A yield of 81% (acetophenone) is obtained using a maximum of 0.4% molar ratio of catalyst relative to the substrate in the presence of TEMPO and in aqueous basic solution, under mild conditions.

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Introduction

Manganese plays an important and diverse role in the biochemistry of many microorganisms, plants and animals. Dinuclear manganese containing active sites are found in a large variety of enzymes that catalyze biological processes,[1] *e.g.* Mn catalases[1c,g–j,2] and arginase,[3] and have received significant attention in bioinorganic chemistry. Besides the biological importance, the relevance in catalysis, under homogeneous and heterogeneous conditions, is also well recognized.[4] Dinuclear manganese complexes of functionalized N_2O_2 Schiff bases, *e.g.*, $[Mn(2\text{-OHsalpn})]_2$ (2-OHsalpn = 1,3-bis(salicylideneamino)-2-propanol), are found to be efficient peroxide disproportionation catalysts in acetonitrile.[5] Mn(III)-salen complexes are efficient catalysts for the oxygenation of heteroatom containing organic compounds[6] and also behave as excellent catalysts for the highly enantioselective asymmetric epoxidation of olefins.[7] Nowadays, microwave-assisted oxidation of alcohols has attracted special attention because it can be a faster, simpler, and more energy efficient technique compared to the conventional methods. Manganese oxides and some simple salts showed a significant activity as catalysts for this process,[8] but, to the best of our knowledge, manganese complexes have not yet been explored as catalysts under these conditions. Recently our group reported that Cu(II) complexes are efficient catalysts in the microwave-assisted oxidation of alcohols.[9] Therefore, the exploration of manganese complexes with suitable N, O donor ligands as catalysts for this reaction would be timely and constitutes an aim of the current work.

On the other hand, manganese complexes are well recognized as magnetic materials,[10] and the polynuclear manganese cluster $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]{\cdot}2CH_3COOH{\cdot}4H_2O$ was reported[11] to be the first single molecule magnet (SMM). SMMs have been synthesized with many different nuclearities, ranging from dinuclear[12] and trinuclear metal complexes[13] to others as large as the Mn 84 wheel.[14]

Therefore, manganese complexes in general and the dinuclear Mn(II,II) compounds in particular with N/O donor ligands

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†CCDC 964300–964304 for **1**·2H_2O, **2**·4H_2O, **4**·H_2O, **5**·2H_2O and **6**·2CH_3OH respectively. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt52774c

have received considerable attention in recent years. In addition, hydrazone Schiff bases form highly stable complexes and can be tuned easily by changing different carbonyl derivatives.[15] In this context, herein we report a series of six dinuclear Mn(II,II) complexes (**1–6**) using three hydrazone Schiff base ligands derived from condensation of three different aromatic acid hydrazides with 2,3-dihydroxy benzaldehyde. This work also focuses on variable temperature magnetic (VTM) susceptibility measurements of three dinuclear Mn(II,II) complexes (**1**, **2** and **6**) to examine the nature of their magnetic behaviour and on their application as catalysts in microwave assisted oxidation of alcohols.

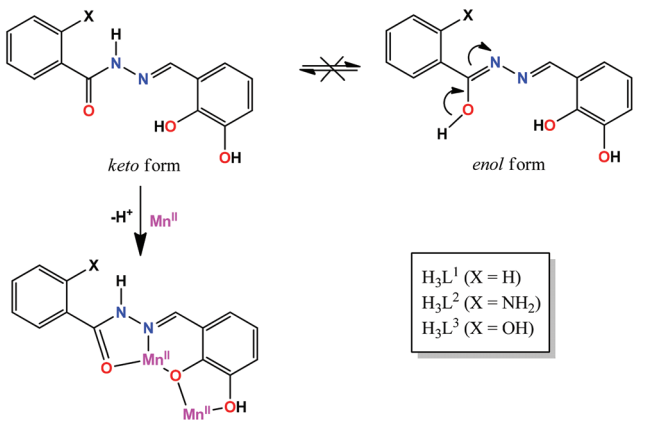
Results and discussion

Three hydrazone Schiff bases (H_3L^1, H_3L^2 and H_3L^3), derived from the reaction of 2,3-dihydroxy benzaldehyde separately with benzohydrazide, 2-aminobenzohydrazide or 2-hydroxybenzohydrazide, respectively, have been used in this study. Hydrazone Schiff bases exhibit keto–enol tautomerism in solution and in the majority of cases the enol form undergoes complexation in the presence of a metal ion.[16] Here a series of mixed-ligand complexes of Mn(II) is reported with these Schiff bases where, in contrast with the above, coordination takes place *via* the keto form (Scheme 1).

Reactions of $Mn(NO_3)_2{\cdot}4H_2O$ with the H_3L^{1-3} compounds, in the presence of pyridine (1 : 1 : 1 mole ratio), in methanol and at room temperature, yield the dinuclear manganese(II) complexes $[Mn(H_2L^1)(py)(H_2O)]_2(NO_3)_2{\cdot}2H_2O$ (**1**·2H_2O), $[Mn(H_2L^2)(py)(CH_3OH)]_2(NO_3)_2{\cdot}4H_2O$ (**2**·4H_2O) and $[Mn(H_2L^3)(py)(H_2O)]_2(NO_3)_2$ (**3**), respectively. The use of excess pyridine in the reaction medium yields dinuclear manganese(II) complexes with two axially coordinated pyridine molecules at each Mn(II) centre, *viz.* $[Mn(H_2L^1)(py)_2]_2(NO_3)_2{\cdot}H_2O$ (**4**·H_2O), $[Mn(H_2L^2)(py)_2]_2(NO_3)_2{\cdot}2H_2O$ (**5**·2H_2O) and $[Mn(H_2L^3)(py)_2]_2(NO_3)_2{\cdot}2CH_3OH$ (**6**·2CH_3OH), respectively. It is noteworthy that attempts of reactions of $Mn(NO_3)_2{\cdot}6H_2O$ with H_3L^{1-3} in methanol in the absence of pyridine did not lead to complex formation, and the presence of an excess of this base did not promote enolization during the desired complexation process. Therefore, pyridine (base/co-ligand) allowed Mn(II) to form stable complexes and promoted exclusively the keto binding mode of coordination of the hydrazino ligands. Such a binding mode was also observed in one Mn(II) complex with a similar type of ligand.[17] We selected the three different types of dinuclear Mn(II,II) complexes **1**, **2** and **6** to examine the nature of magnetic interactions and also to study their catalytic properties towards microwave assisted oxidation of alcohols.

General description of the crystal structures

X-ray quality crystals of the compounds were obtained upon slow evaporation of their methanolic solutions, at room temperature. The crystallographic data and processing parameters are summarized in Table 1, representative plots are



Scheme 1 Mode of coordination of the ligands $(H_2L^{1-3})^-$ in the dinuclear Mn(II,II) complexes.

Table 1 Crystal data and structure refinement details of complexes **1**·2H_2O, **2**·4H_2O, **4**·H_2O, **5**·2H_2O and **6**·2CH_3OH

	1·2H_2O	**2**·4H_2O	**4**·H_2O	**5**·2H_2O	**6**·2CH_3OH
Empirical formula	$C_{38}H_{40}Mn_2N_8O_{16}$	$C_{40}H_{42}Mn_2N_{10}O_{18}$	$C_{48}H_{44}Mn_2N_{10}O_{13}$	$C_{48}H_{48}Mn_2N_{12}O_{14}$	$C_{50}H_{50}Mn_2N_{10}O_{16}$
Formula weight	974.66	1068.78	1078.81	1126.86	1156.88
Temp./K	150	296	296	150	150
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	*Pbca*	*C*2/*c*	*C*2/*c*	$P\bar{1}$	$P2_1/c$
a/Å	11.1784(7)	27.7167 (12)	12.8357 (4)	10.5455 (8)	12.8509 (6)
b/Å	18.6890(9)	10.8872 (5)	17.3807 (5)	10.5706 (9)	18.0597 (9)
c/Å	19.5725(9)	19.6740 (10)	23.5331 (6)	11.9344 (10)	12.2873 (6)
α/°	90	90	90	95.750 (5)	90
β/°	90	126.3820(10)	100.2330 (10)	106.408 (5)	108.603 (2)
γ/°	90	90	90	103.690 (6)	90
V (Å^3)	4089.0(4)	4779.6 (4)	5166.6 (3)	1219.84 (17)	2702.7 (2)
Z	4	4	4	1	2
D_{calc} (g cm^{-3})	1.583	1.474	1.387	1.534	1.422
μ(Mo Kα) (mm^{-1})	0.702	0.612	0.560	0.599	0.545
Rfls. collected/unique/observed	18 229/4153/2382	26 060/4103/2809	17 872/3953 /3062	9698/4154/2075	20 228/5524/3729
R_{int}	0.0929	0.0735	0.0322	0.1010	0.0504
Final R_1[a], wR_2[b] ($I \geq 2\sigma$)	0.0519, 0.1018	0.0530, 0.1469	0.0568, 0.1456	0.0868, 0.2086	0.0442, 0.1061
Goodness-of-fit on F^2	0.973	1.044	1.022	1.023	1.027

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR(F^2) = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^4]^{1/2}$.

displayed in Fig. 1, and selected dimensions are presented in Table 2. Relevant hydrogen bond interactions are shown in Table 3.

X-ray single-crystal analyses of the dinuclear complexes **1**·2H_2O, **2**·4H_2O, **4**·H_2O, **5**·2H_2O and **6**·2CH_3OH show that their asymmetric units contain half of the molecules, *viz.* one manganese(II) cation with one coordinated ligand, one pyridine and one water (or one methanol) molecule (**1**·2H_2O or **2**·4H_2O, respectively), or one manganese(II) cation with two pyridine moieties (**4**·H_2O, **5**·2H_2O and **6**·2CH_3OH). The asymmetric units also contain one (**1**·2H_2O, **4**·H_2O and **5**·2H_2O) or two (**2**·4H_2O) water molecules or a methanol molecule (**6**·2CH_3OH). All the structures contain crystallographically imposed inversion centres in the middle of the Mn1–Mn1^i bonds, and therefore in the heart of the respective Mn_2O_2 planes. The Schiff bases act as monoanionic and tetradentate ONOO equatorial ligands, coordinating to one of the metal centres *via* the keto oxygen, the hydrazino nitrogen and the deprotonated 2-hydroxyl oxygen, and to the other metal cation through the phenoxy group and the 3-hydroxyl moiety. Thus, each structure exhibits two μ-O bridges which link the two manganese(II) centres which, by themselves, display hepta coordination and present distorted pentagonal bipyramidal geometries. The axial positions are occupied by the pyridine nitrogen atoms and the water or the methanol oxygen atoms, as appropriate.

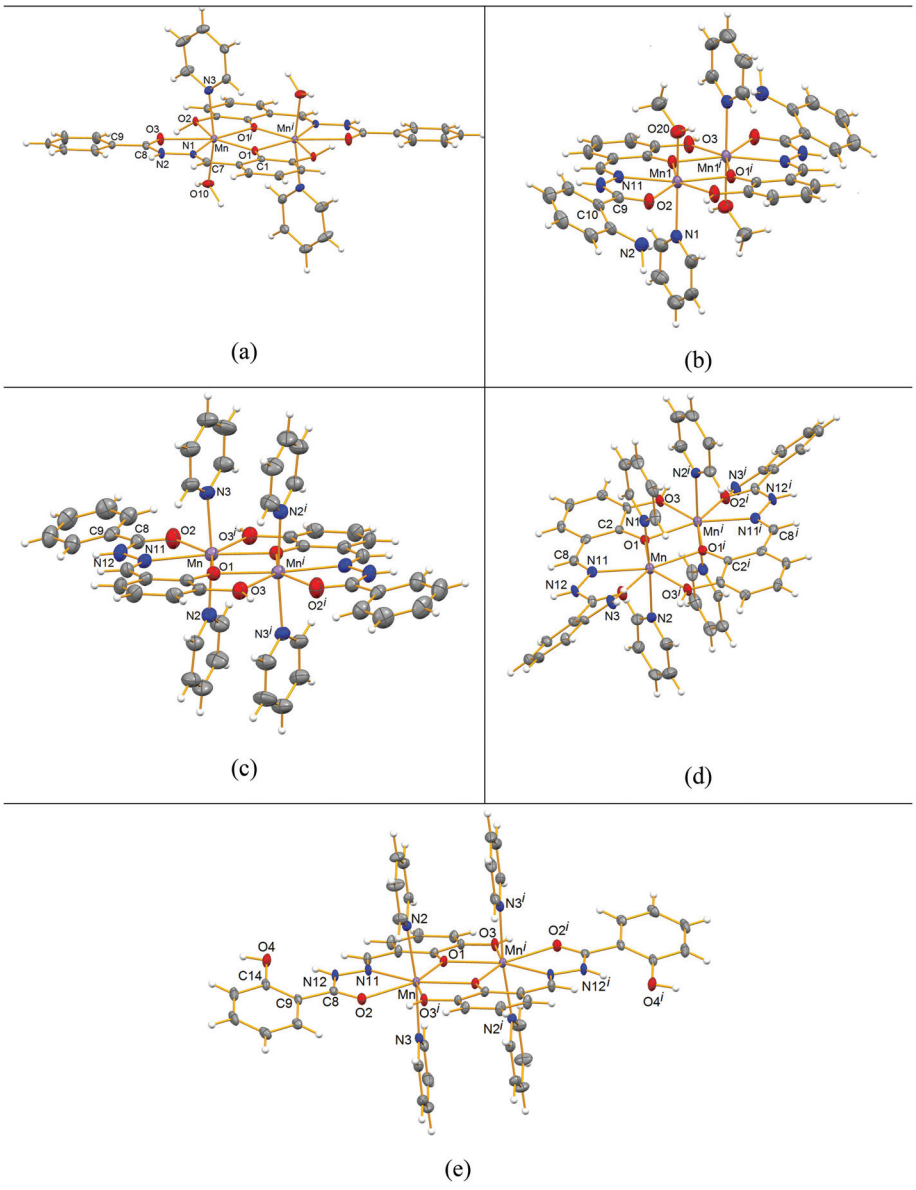


Fig. 1 Thermal ellipsoid plots (drawn at 30% probability level) of complexes (a) **1**·2H_2O, (b) **2**·4H_2O, (c) **4**·H_2O, (d) **5**·2H_2O and (e) **6**·2CH_3OH with the partial atom labeling scheme. Nitrate anions, water and methanol molecules are omitted for clarity. Symmetry codes to generate equivalent atoms: (i) –*x*,–*y*, 1 – *z* (**1**·2H_2O), 1 – *x*, 1 – *y*, 2 – *z* (**2**·4H_2O), 1.5 – *x*, 1/2 – *y*, 1 – *z* (**4**·H_2O), 1 – *x*, 1 – *y*, 2 – *z* (**5**·2H_2O), –*x*, –*y*, –*z* (**6**·2CH_3OH).

Table 2 Selected bond distances (Å) and angles (°) in complexes **1**·2H_2O, **2**·4H_2O, **4**·H_2O, **5**·2H_2O and **6**·2CH_3OH[a]

Parameter	**1**·2H_2O	**2**·4H_2O	**4**·H_2O	**5**·2H_2O	**6**·2CH_3OH
Mn environment	N_2O_5	N_2O_5	N_3O_4	N_3O_4	N_3O_4
N–N	1.382(4)	1.391(4)	1.451(4)	1.385(9)	1.375(3)
Mn–N_{hyd}	2.340(3)	2.350(3)	2.412(3)	2.345(6)	2.336(2)
Mn–N_{Pyr}	2.254(3)	2.284(4)	2.310(3)	2.282(7)	2.267(2)
			2.320(3)	2.295(7)	2.282(2)
Mn–O_{core}	2.140(3)	2.160(2)	2.216(2)	2.146(5)	2.1802(16)
	2.288(2)	2.269(2)	2.375(2)	2.290(5)	2.2672(16)
Mn–O_{ol}	2.297(3)	2.282(2)	2.329(3)	2.276(5)	2.2925(17)
Mn–O_{Keto}	2.335(3)	2.340(2)	2.412(3)	2.291(6)	2.3291(18)
Mn–$O_{H2O(MeOH)}$	2.163(3)	2.200(2)	—	—	—
∠N_{pyr}–Mn–N_{pyr}	—	—	173.49(12)	175.9(3)	173.86(8)
∠N_{pyr}–Mn–$O_{H2O(MeOH)}$	166.89(13)	172.83(11)	—	—	—
∠O_{core}–Mn–O_{core}	74.30(9)	75.24(9)	73.39(11)	74.4(2)	74.47(7)
∠ Mn–O_{core}–Mn	105.69(9)	104.76(9)	106.61(10)	105.63(19)	105.53(7)
∠P_{pyr}/P_{pyr}	—	—	8.87	4.04	3.02
∠P_{core}/P_{phenyl}	9.27	30.05	10.11	35.28	22.04
Mn⋯Mn	3.5306(8)	3.5088(10)	3.6829(7)	3.5356(18)	3.5413(5)

[a] N_{hyd} = coordinated N-hydrazino atom; N_{pyr} = coordinated N-pyridine atom. O_{ol}, O_{keto} and $O_{H2O(MeOH)}$ refer to the deprotonated, keto and water (or methanol) O-atoms, respectively. P_{core}, P_{pyr} and P_{phenyl} represent the mean planes of the $Mn_2(\mu\text{-}O)_2$ cores, the pyridine rings and the non-coordinated phenyl ring, in this order.

Table 3 Hydrogen bond geometry (Å, °) in the manganese compounds **1**·2H_2O, **2**·4H_2O, **4**·H_2O, **5**·2H_2O and **6**·2CH_3OH[a]

Compound	D–H⋯A	*d*(H⋯A)	*d*(D⋯A)	∠(D–H⋯A)	Symmetry operation
1·2H_2O	N2–H2⋯O20	2.17(3)	2.982(4)	168(4)	—
	O2–H2O⋯O12	1.794(19)	2.675(4)	173(3)	$1/2 - x, 1/2 + y, z$
	O10–H10A⋯O11	1.984(19)	2.851(4)	175(3)	$-1/2 + x, 1/2 - y, -z$
	O10–H10B⋯O13	1.87(2)	2.779(5)	176(3)	$-1 + x, y, z$
	O20–H20B⋯O13	2.11(3)	2.855(4)	142(3)	$-1/2 + x, y, 1/2 - z$
2·4H_2O	N12–H12A⋯O13	2.18	2.907(4)	142.6	$1/2 - x, -1/2 + y, 1/2 - z$
	O3–H3⋯O1W	1.75	2.651(4)	161.2	$1/2 + x, 1/2 - y, -1/2 + z$
	O20–H20⋯O3W	1.94	2.769(9)	148.0	$1/2 + x, 1/2 + y, z$
	O20–H20⋯O2W	2.00	2.770(5)	138.6	$1/2 + x, 1/2 + y, z$
	N2–H2B⋯O2	2.22(8)	2.732(4)	116(6)	*Intra*
4·H_2O	N12–H12A⋯O20W	2.14	2.913(5)	149.8	—
	O20W–H20A⋯O41	1.90(5)	2.819(9)	154(10)	—
	O20W–H20A⋯O40	2.05(8)	2.884(7)	141(10)	—
	O3–H3A⋯O42	1.81	2.728(5)	170.2	$x, -y, -1/2 + z$
5·2H_2O	N3–H3A⋯O2	2.110	2.735(9)	128.0	*Intra*
	N3–H3B⋯O11	2.030	2.880(10)	163.7(5)	$1 - x, 2 - y, 1 - z$
	N12–H12A⋯O12	2.13(8)	2.876(10)	155(9)	$1 + x, y, z$
	O10–H10B⋯O11	1.99(4)	2.876(13)	158(7)	$1 - x, 1 - y, 1 - z$
	O10–H10A⋯N3	2.08(4)	2.920(10)	153(6)	$1 - x, 1 - y, 1 - z$
	O3–H3⋯O10	1.69	2.594(9)	157.8	$x, y, -1 + z$
6·2CH_3OH	N12–H12A⋯O4	2.01	2.646(3)	128.6	*Intra*
	O20–H20⋯O13	1.98	2.822(3)	174.6	—
	O3–H3O⋯O20	1.71	2.628(2)	174.53(12)	$1 + x, y, 1 + z$
	O4–H4O⋯O12	1.74(3)	2.692(3)	173(3)	—

[a] Only the strongest classical hydrogen bond interactions are shown (D⋯A distances lower than 3 Å).

Although run at low (**1**, **5** and **6**) and at room temperatures (**2** and **4**), and considering the similarities between the ligands and the obtained structures, some general comparisons can tentatively be made (Table 2). The bond distances of 1.380(4)–1.392(4) Å for the N–N groups suggest their single bond hydrazino character. The Mn–$N_{hydrazino}$ bond distances [average 2.357(3) Å] are longer than the Mn–$N_{pyridine}$ bonds [average 2.287(4) Å] and, for those complexes with two pyridine ligands per metal cation (**4**·H_2O, **5**·2H_2O and **6**·2CH_3OH), one of the bonds slightly exceeds the other (by 0.010–0.016 Å). The N_{pyr}–Mn–N_{pyr} groups are nearly linear (minimum of 173.49(12)° for **4**·H_2O) and exceed the N_{pyr}–Mn–$O_{H2O(MeOH)}$ values of 166.95(12)° (**1**·2H_2O) and 172.80(11)° (**2**·4H_2O). The latter values are intimately related with the H-bond interactions in which the water and methanol ligands are involved (see below).

In the $Mn_2(\mu\text{-}O)_2$ cores the Mn–O–Mn angles range from 104.79(9) to 106.61(10)° and the O–Mn–O angle assumes values of 73.39(11)–75.21(9)° (Table 2); expectedly, the widening of the former leads to a tapering of the latter. Comparing the various

Mn–O bond distances, it is observed that those involving the keto oxygen are larger, the only exception being **5**·2H_2O where this parameter is similar to the one of the Mn–O_{core}.

The mode of coordination of the $(H_2L^{1-3})^-$ ligands to the Mn(II) cation in the complexes of this study is also worth discussing, in what concerns their planarity here evidenced by the twistings of the phenyl rings (denoted as P_{phenyl}, Table 2) relative to the plane of the $Mn_2(\mu\text{-}O)_2$ core (symbolized by P_{core}, Table 2). While for complexes **1**·2H_2O and **4**·H_2O, that parameter assumes values of 9.27 and 10.11°, respectively, for complexes **2**·4H_2O and **5**·2H_2O, which possess NH_2 substituents in those phenyl groups, it adopts values as high as 30.05 and 35.28°, in this order; complex **6**, with an OH substituent, presents an intermediate value (22.04°). These twistings are certainly related to hydrogen bond interactions (Table 3) involving such substituents which, in the relevant cases (**2**·4H_2O, **5**·2H_2O and **6**·2CH_3OH), act as donor groups towards nitrate. Moreover, the NH_2 phenyl moieties in **2**·4H_2O and **5**·2H_2O are directed towards the coordinated keto atom and ultimately interact with it; in contrast, the OH group in **6** is engaged with the H-atom of the hydrazine set.

Extensive hydrogen bond interaction can be found in all the compounds of this work (Fig. 2, 3 and Table 3). Such interactions result from the presence of coordinated (in **1**·2H_2O) or free (in **1**·2H_2O, **2**·4H_2O, **4**·H_2O and **5**·2H_2O) water molecules which act both as proton donors (usually to nitrate anions; eventually to the N-aniline moiety in **2**·4H_2O and **5**·2H_2O) and as proton acceptors (from coordinated methanol in **2**·4H_2O, HN-aniline protons in **4**·H_2O or the protonated phenol group in **2**·4H_2O and **5**·2H_2O). These interactions are usually strong [d(D···A) distances in the 2.594(9)–2.982(4) Å range, and ∠(D–H···A) between 116 and 176°], the most intense one [d(D···A) 2.594(9) Å; ∠(D–H···A) 157.8°] being found in **5**·2H_2O and concerning the coordinated OH phenol group which acts as a donor to a free water molecule. It is compound **2**·4H_2O, which presents four crystallization water molecules per unit cell, that discloses the most intricate network, as expressed by the higher number of H-bonds detected (Table 3).

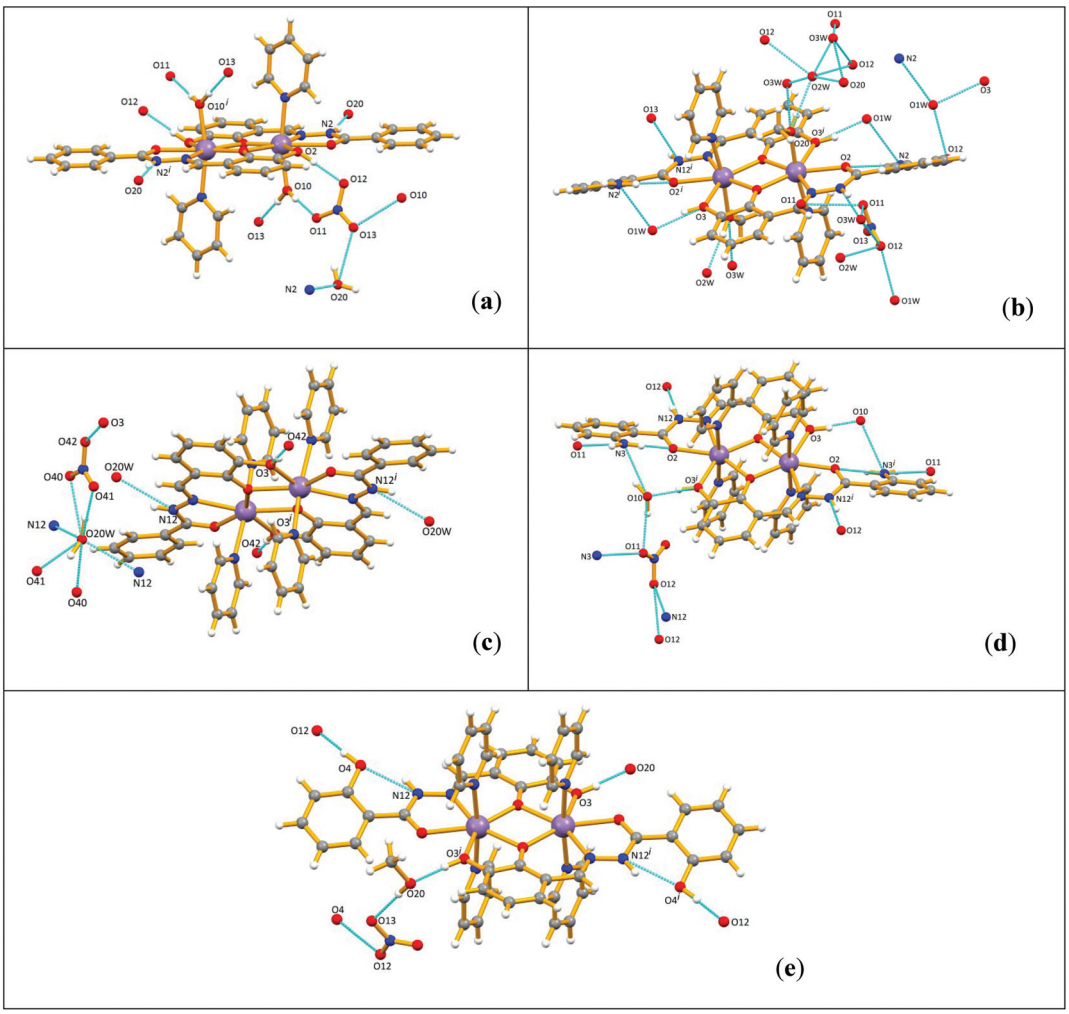


Fig. 2 Hydrogen bond interactions (in dashed light blue line) for complexes (a) **1**·2H_2O, (b) **2**·4H_2O, (c) **4**·H_2O, (d) **5**·2H_2O and (e) **6**·2CH_3OH. Symmetry operations are given in Table 3.

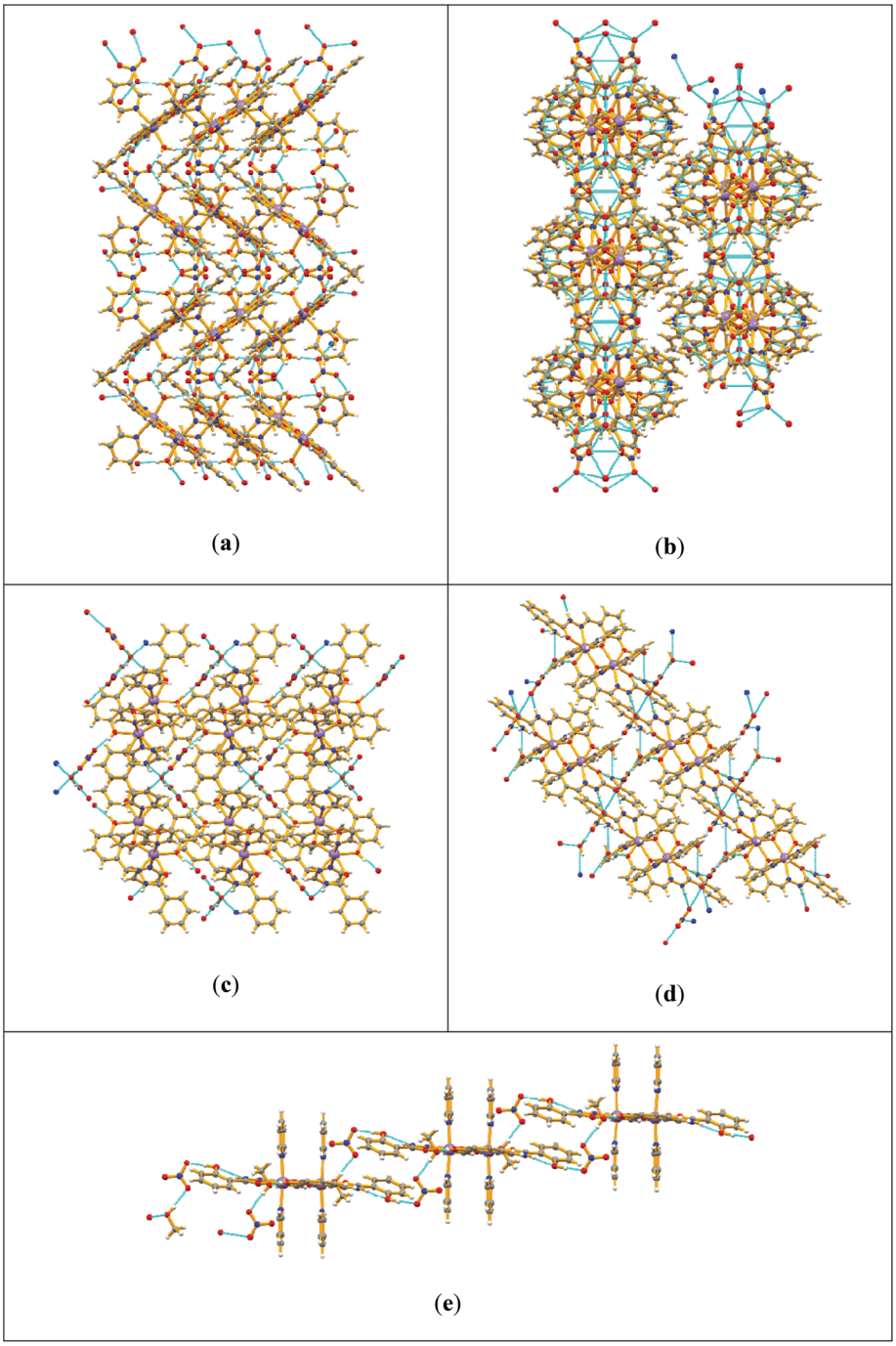


Fig. 3 Packing diagram of complexes (a) **1**·2H_2O, (b) **2**·4H_2O, (c) **4**·H_2O, (d) **5**·2H_2O and (e) **6**·2CH_3OH highlighting the hydrogen bond interactions (in dashed light blue line).

Magnetism

The temperature dependence of the magnetic susceptibilities of **1**, **2** and **6** has been investigated. The thermal variation of χ and χT for three complexes in the temperature range 2–300 K is shown in Fig. 4. The room temperature $\chi_M T$ values of 9.43 cm^3 K mol^{-1} for **1**, 9.04 cm^3 K mol^{-1} for **2** and 9.38 cm^3 K mol^{-1} for **6** are a little larger than the value expected for two non-coupled Mn(II) ions (8.655 cm^3 K mol^{-1}, assuming g = 2.0). The values of $\chi_M T$ almost remain constant above 50 K on cooling and then deeply decrease reaching a minimum of 0.88 cm^3 K mol^{-1} for **1**, 0.75 cm^{-3} K mol^{-1} for **2** and 0.61 cm^{-3} K mol^{-1} for **6** at 2 K, suggesting an overall antiferromagnetic interaction between Mn^{2+} ions in these complexes. The binuclear Mn(II) model utilized[17] for $[Mn^{II}_2(HL)_2(CH_3OH)_2(py)_2](ClO_4)_2$·2py was adopted to simulate the magnetic susceptibility of **1**. Eqn (1) is derived from the Hamiltonian $H = -JS_1S_2$. Here, N, k and β constants have their usual meaning.

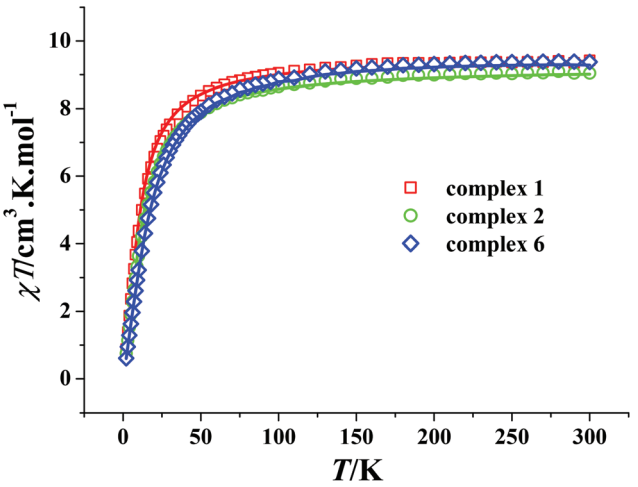


Fig. 4 Temperature dependence of the $\chi_M T$ product for complexes **1**, **2** and **6** in the temperature range of 2–300 K.

$$\chi = 2Ng^2\beta^2 A/kTB \quad (1)$$

where

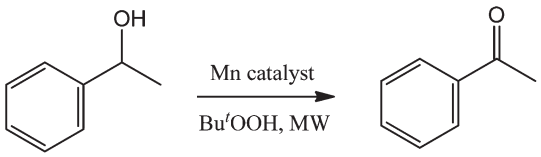
$$A = \exp(J/kT) + 5\exp(3J/kT) + 14\exp(6J/kT) + 30\exp(10J/kT) + 55\exp(15J/kT)$$

$$B = 1 + 3\exp(J/kT) + 5\exp(3J/kT) + 7\exp(6J/kT) + 9\exp(10J/kT) + 11\exp(15J/kT)$$

The best fitting gives $J = -1.45$ cm^{-1}, $g = 2.06$, $R = 2.65 \times 10^{-5}$ for **1**, $J = -2.05$ cm^{-1}, $g = 2.02$, $R = 7.87 \times 10^{-5}$ for **2**, and $J = -1.69$ cm^{-1}, $g = 2.06$, $R = 5.35 \times 10^{-5}$ for **6**. These J values are a little more negative than that of $[Mn^{II}_2(HL)_2(CH_3OH)_2(py)_2](ClO_4)_2{\cdot}2py$ (-0.98 cm^{-1}), which could be ascribed to the larger Mn–O–Mn angles of **1** (105.68°), **2** (104.81°) and **6** (105.54°) in comparison with $[Mn^{II}_2(HL)_2(CH_3OH)_2(py)_2](ClO4)_2{\cdot}2py$ (mean value of 103.83°).

Catalysis

The manganese complexes **1**, **2** and **6** have been tested as catalysts (or catalyst precursors) for the oxidation of common secondary alcohols (usually 1-phenylethanol) to the respective ketones using *tert*-butylhydroperoxide (Bu^tOOH, TBHP) (2 eq.) as an oxidizing agent, under typical conditions of 80 °C, low power (10 W) microwave irradiation (MW), 3 h reaction time and in the absence of any added solvent (Scheme 2 for the oxidation of 1-phenylethanol). Selected results are summarized in Table 4.



Scheme 2 Added solvent-free oxidation of 1-phenylethanol to acetophenone.

Under typical conditions, yields up to 30% are obtained, but the presence of 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO) (see below) can lead to the yield increase up to 81% (entry 20, Table 4). Compound **6** appears to be a more active catalyst precursor than **1** or **2**. This eventually can be accounted for by the presence of the basic amino-substituent at the Schiff base ligand. Amino groups can have a favourable effect on oxidation catalysis, as was observed[18] for various catalytic systems in peroxidative alkane oxidations with catalysts bearing aminoalcohol ligands.

The influence of the amount of catalyst **6** was studied (entries 6–10, Table 4, Fig. 5). Its increase results in a yield enhancement, *e.g.*, from 6% to 32% upon changing the amount of catalyst from 5 μmol (0.1 mol% *vs.* substrate) to 100 μmol (2 mol% *vs.* substrate). As expected, the increase of the catalyst amount results in a corresponding TON (moles of product per mole of catalyst) lowering from 51 to 12. Blank tests (in the absence of any catalyst) were performed under common reaction conditions and no significant conversion was observed.

It is known[9,19] that MW can provide a more efficient synthetic method than conventional heating, allowing us to achieve the same yield in a shorter time and/or to improve the yield and/or selectivity. A favourable effect of MW is also observed in this study even at the low power of 10 W, as reported[9] for other systems. Hence, for example, the product yield increases from 18% (entry 23) to 81% (entry 20), in the presence of TEMPO/K_2CO_3 (see below), upon MW irradiation, the other conditions being the same, although in the absence of such additives a lower yield enhancement was observed (entry 22 *vs.* 3).

The use of hydrogen peroxide (30% aqueous solution) instead of TBHP results in a marked yield lowering from 14% to 2% (entries 8 and 12, respectively, Table 4), in accord with the expected decomposition of H_2O_2 under the applied reaction conditions (80 °C). The use of more oxidant does not lead to a better conversion (entries 8 and 11, Table 4).

Performing the reaction in the presence of acetonitrile does not change significantly the yield, *e.g.* for the 1-phenylethanol oxidation in the presence of **6** in acetonitrile, the yield decreases from 14%, under added solvent-free conditions (entry 8, Table 4), to 11% in NCMe (entry 15, Table 4), whereas the use of water as a solvent results in a more significant yield reduction from 14%, without any added solvent, to 1% in water (entry 16, Table 4), under the same reaction conditions. In contrast, the use of a basic solution of 1 M K_2CO_3 (entry 17, Table 4) results in a significant increase of the conversion of the alcohol to the ketone compared to simple water (from 1% only in water to 32% in basic solution) or even to the added solvent-free system (14% yield, entry 3, Table 4). The role of basic additives, which facilitate the deprotonation of the alcohol, has already been observed in other cases.[20,21]

The relevance of the ligands to the catalytic activity of the metal complexes is shown by testing also the catalytic

Table 4 Oxidation of selected secondary alcohols using **1**, **2** and **6** as catalyst precursors[a]

Entry	Catalyst	Substrate	Reaction time [h]	Catalyst amount [μmol]	TON[b]	Yield[c] [%]
1	**6**	1-Phenylethanol	0.5	20	23	6
2	**6**	1-Phenylethanol	1	20	27	7
3	**6**	1-Phenylethanol	3	20	36	14
4	**6**	1-Phenylethanol	6	20	50	20
5	**6**	1-Phenylethanol	15	20	75	31
6	**6**	1-Phenylethanol	3	5	51	6
7	**6**	1-Phenylethanol	3	10	36	11
8	**6**	1-Phenylethanol	3	20	34	14
9	**6**	1-Phenylethanol	3	40	18	17
10	**6**	1-Phenylethanol	3	100	12	32
11[d]	**6**	1-Phenylethanol	3	20	31	14
12[e]	**6**	1-Phenylethanol	3	20	7	2
13[f]	**6**	1-Phenylethanol	3	20	1	2
14[g]	**6**	1-Phenylethanol	3	20	—	—
15[h]	**6**	1-Phenylethanol	3	20	23	11
16[i]	**6**	1-Phenylethanol	3	20	2	1
17[j]	**6**	1-Phenylethanol	3	20	80	32
18[k]	**6**	1-Phenylethanol	3	20	59	37
19[l]	**6**	1-Phenylethanol	3	20	49	36
20[m]	**6**	1-Phenylethanol	3	20	203	81
21[k]	**6**	1-Phenylethanol	3	100	36	73
22[n]	**6**	1-Phenylethanol	3	20	27	9
23[m,n]	**6**	1-Phenylethanol	3	20	34	18
24[o]	—	1-Phenylethanol	3	—	9	4
25	**6**	Cyclohexanol	3	20	21	28
26	**6**	2-Octanol	3	20	74	22
27	**6**	3-Octanol	3	20	37	5
28	**2**	1-Phenylethanol	3	10	38	8
29	**2**	1-Phenylethanol	3	20	26	11
30	**2**	1-Phenylethanol	15	20	29	12
31[m]	**2**	1-Phenylethanol	3	20	77	31
32	**1**	1-Phenylethanol	3	20	37	9
33	**1**	1-Phenylethanol	6	20	39	16
34	**1**	1-Phenylethanol	15	20	58	23
35[m]	**1**	1-Phenylethanol	3	20	106	42
36	**1**	1-Phenylethanol	3	50	15	30
37[m,p]	**$Mn(NO_3)_2{\cdot}4H_2O$**	1-Phenylethanol	3	40	15	12

[a] Reaction conditions unless stated otherwise: 5 mmol of substrate, 1–100 μmol of catalyst (0.02–1.4 mol% *vs.* substrate), 10 mmol of TBHP (2 eq.), 80 °C, 3 h reaction time, microwave irradiation (10 W). [b] Turnover number = number of moles of product per mole of catalyst. [c] Moles of ketone product per mole of alcohol. [d] 20 mmol of TBHP (4 eq.). [e] H_2O_2 30% aqueous solution instead of TBHP. [f] In the presence of Ph_2NH. [g] In the presence of $CBrCl_3$. [h] In NCMe. [i] In H_2O. [j] In K_2CO_3 aqueous solution (1 M). [k] In the presence of TEMPO (0.125 mmol). [l] In the presence of TEMPO (0.250 mmol). [m] In the presence of TEMPO (0.125 mmol) and in 1 M K_2CO_3 aqueous solution. [n] Without microwave irradiation. [o] TEMPO as a catalyst. [p] Included for comparative purposes.

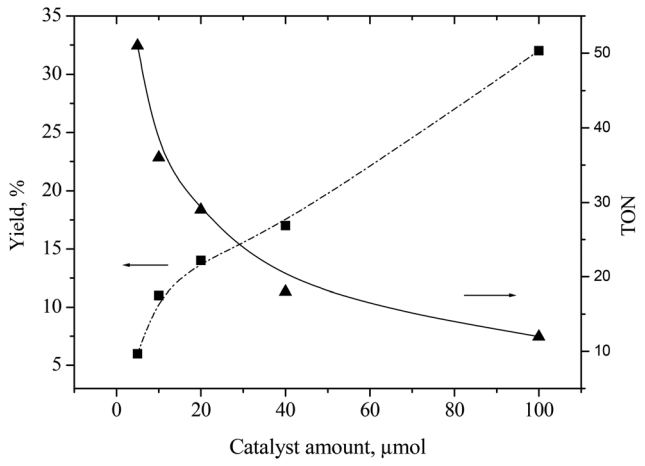


Fig. 5 Effect of the amount of catalyst **6** on the yield (dotted line) and turnover number (TON) (solid line) for the oxidation of 1-phenylethanol to acetophenone.

performance of $Mn(NO_3)_2{\cdot}4H_2O$ in the oxidation of 1-phenylethanol and comparing it, for the same reaction conditions, with those of **1**, **2** and **6**. Hence, in the presence of the TEMPO/K_2CO_3 combination, the use of that salt leads to a 12% yield of acetophenone (entry 37, Table 4), which is much lower than those achieved in the presence of **1**, **2** and **6** (42, 31 and 81%; entries 35, 31 and 20, Table 4) under the same experimental conditions.

The addition to the reaction mixture of Ph_2NH or $CBrCl_3$, well known oxygen- or carbon radical traps, respectively,[22] results in an important yield drop, compared to the reaction carried out under the same conditions (20 μmol, 80 °C, MW, 3 h) but in the absence of a radical trap. This suggests the generation of oxygen and carbon radicals in the reaction, which are trapped by those radical scavengers. The mechanism may involve coordination of 1-phenylethanol followed by metal-centred dehydrogenation and oxidation of the alcohol

through hydrogen abstraction or one-electron oxidation processes.[21a,d]

In an attempt to increase the activity of **1**, **2** and **6** in solvent-free MW-assisted peroxidative oxidation of 1-phenylethanol, we have investigated the influence of 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO), a nitroxyl radical that is a known[9b,21a,c,d,23] promoter of oxidation catalysis of alcohols. In accord, a significant yield increase was observed for the 1-phenylethanol oxidation in the presence of **6** (from 14% in the absence of TEMPO to *ca.* 37% in its presence; entries 8, 18 and 19, Table 4, respectively).

The reactions performed in the presence of TEMPO (0.125 mmol) and in 1 M K_2CO_3 aqueous solution (entries 35, 31 and 20, Table 4) give the highest yields of 42, 31 and 81% for **1**, **2** and **6**, respectively (Fig. 6).

Recently, our group reported some efficient systems involving copper(II) triazapentadienate,[9a,b] bis- and tris-pyridyl amino and imino thioether Cu and Fe complexes[9c] for the MW-assisted oxidation of secondary alcohols to the corresponding ketones, the *in situ* generated copper(II)-diimine complexes towards the TEMPO-mediated oxidation of benzylic alcohols in aqueous media[21a] and copper(II) complexes containing arylhydrazones from methylene-active nitriles towards the selective oxidation of primary and secondary alcohols to the corresponding carbonyl compounds.[9b] The above catalytic systems lead to higher yields and/or TONs than those of this work. Other manganese-based systems were reported for alcohols oxidation, namely the silica-supported manganese dioxide (MnO_2) used in the oxidation of benzyl alcohol under solvent-free conditions,[8b] which yielded acetophenone in 88%, under MW for 20 s, but required an excess of MnO_2 relative to the substrate (5 : 1 molar ratio), while in our system we achieved 81% yield using a maximum of 0.4% molar ratio of the catalyst relative to the substrate.

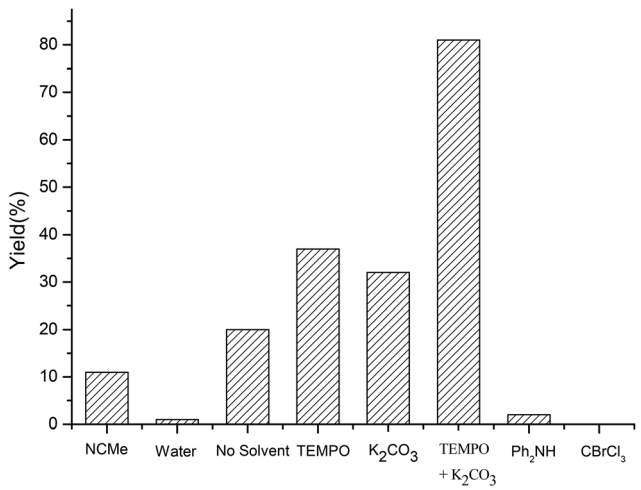


Fig. 6 Influence of different solvents and additives on the yield of acetophenone from oxidation of 1-phenylethanol.

Experimental section

General materials and procedures

All synthetic work was performed in air. The reagents and solvents were obtained from commercial sources and used as received, *i.e.*, without further purification or drying. $Mn(NO_3)_2 \cdot 4H_2O$ has been used as a precursor for the synthesis of complexes **1–6**. C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Infrared spectra (4000–400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX or a Jasco FT/IR-430 instrument in KBr pellets; wavenumbers are in cm^{-1}. Gas chromatographic (GC) measurements were carried out using a FISONS Instruments GC 8000 series gas chromatograph with a FID detector and a capillary column (DB-WAX, column length: 30 m; internal diameter: 0.32 mm). The temperature of injection was 240 °C. The initial temperature of the column was maintained at 120 °C for 1 min, and then raised at 10 °C min^{-1} up to 200 °C, and held at this temperature for 1 min. Helium was used as the carrier gas. The magnetic susceptibility measurements were carried out on polycrystalline samples with a Quantum Design MPMS-XL5 SQUID magnetometer in the temperature range of 2–300 K at an applied field of 2000 Oe. Diamagnetic corrections were estimated from Pascal's constants for all constituent atoms.[24] The catalytic investigations under microwave irradiation (10 W) were performed in a focused microwave CEM Discover reactor (10 mL, 13 mm diameter) fitted with a rotational system and an IR detector of temperature.

Synthesis of the pro-ligands H_3L^1–H_3L^3. The Schiff base pro-ligands (2,3-dihydroxybenzylidene)benzohydrazide (H_3L^1), 2-amino-(2,3-dihydroxybenzylidene)benzohydrazide (H_3L^2) and (2,3-dihydroxybenzylidene)-2-hydroxybenzohydrazide (H_3L^3) (Scheme 1) were prepared by a reported method[25] upon condensation of the corresponding aromatic acid hydrazides and 2,3-dihydroxybenzaldehyde.

Synthesis of dinuclear Mn(II,II) complexes (1–6)

*$[Mn(H_2L^1)(py)(H_2O)]_2(NO_3)_2 \cdot 2H_2O$ (**1**·2H_2O).* To a 15 mL methanol solution of H_3L^1 0.256 g (1.00 mmol), 0.256 g (1.02 mmol) of $Mn(NO_3)_2 \cdot 4H_2O$ was added and the reaction mixture was stirred for 15 min at room temperature. Thereafter, 0.08 g (1.01 mmol) of pyridine was added and stirring was continued for 1 h. The resulting yellow solution was filtered and the filtrate was kept in open air at room temperature for crystallization. After 3 days, single crystals suitable for X-ray diffraction were isolated.

Yield 74%. Anal. calcd for $C_{38}H_{36}N_8O_{14}Mn_2$ (**1**): C, 48.63; H, 3.87; N, 11.94. Found: C, 48.56; H, 3.84; N, 11.86. IR (KBr; cm^{-1}): 3386, 3224 ν(OH), 3058 ν(NH), 1638, 1613 ν(C=N), 1384 $\nu(NO_3^-)$, and 1071 ν(N–N).

Complexes **2** and **3** have been synthesized using the same procedure.

*$[Mn(H_2L^2)(py)(CH_3OH)]_2(NO_3)_2 \cdot 4H_2O$ (**2**·4H_2O).* Yield 68%. Anal. calcd for $C_{40}H_{42}N_{10}O_{14}Mn_2$ (**2**): C, 48.20; H, 4.25; N, 14.05. Found: C, 48.12; H, 4.21; N, 13.97. IR (KBr; cm^{-1}): IR (KBr; cm^{-1}): 3364, 3242 ν(OH), 2988 ν(NH), 1632, 1608 ν(C=N), 1384 $\nu(NO_3^-)$, and 1066 ν(N–N).

*[Mn(H$_2$L^3)(py)(H$_2$O)]$_2$(NO$_3$)$_2$ (**3**).* Yield 78%. Anal. calcd for $C_{38}H_{36}N_8O_{16}Mn_2$ (**3**): C, 47.02; H, 3.74; N, 11.54. Found: C, 46.96; H, 3.69; N, 11.47. IR (KBr; cm^{-1}): 3394, 3224 ν(OH), 2956 ν(NH), 1642, 1614 ν(C=N), 1383 ν(NO_3^-), and 1064 ν(N–N).

Complexes **4–6** have been synthesized using the same procedure as that mentioned above but only the amount of pyridine was taken in excess (0.032 g, 4.04 mmol).

*[Mn(H$_2$L^1)(py)$_2$]$_2$(NO$_3$)$_2$·H$_2$O (**4**·H$_2$O).* Yield 78%. Anal. calcd for $C_{48}H_{42}N_{10}O_{12}Mn_2$ (**4**): C, 54.35; H, 3.99; N, 13.20. Found: C, 54.29; H, 3.95; N, 13.12. IR (KBr; cm^{-1}): 3346, 3216 ν(OH), 2984 ν(NH), 1646, 1618 ν(C=N), 1384 ν(NO_3^-), and 1064 ν(N–N).

*[Mn(H$_2$L^2)(py)$_2$]$_2$(NO$_3$)$_2$·2H$_2$O (**5**·2H$_2$O).* Yield 78%. Anal. calcd for $C_{48}H_{44}N_{12}O_{12}Mn_2$ (**5**): C, 52.85; H, 4.07; N, 15.41. Found: C, 52.79; H, 4.02; N, 15.34. IR (KBr; cm^{-1}): 3399, 3236 ν(OH), 2924 ν(NH), 1632, 1614 ν(C=N), 1384 ν(NO_3^-), and 1068 ν(N–N).

*[Mn(H$_2$L^3)(py)$_2$]$_2$(NO$_3$)$_2$·2CH$_3$OH (**6**·2CH$_3$OH).* Yield 76%. Anal. calcd for $C_{48}H_{42}N_{10}O_{14}Mn_2$ (**6**): C, 52.76; H, 3.87; N, 12.82. Found: C, 52.68; H, 3.84; N, 12.77. IR (KBr; cm^{-1}): 3380, 3214 ν(OH), 2986 ν(NH), 1618 ν(C=N), 1383 ν(NO_3^-), and 1065 ν(N–N).

X-ray structure determinations

Crystals of **1**·2H$_2$O, **5**·2H$_2$O and **6**·2CH$_3$OH were immersed in cryo-oil, mounted in a nylon loop and measured at a temperature of 150 K; crystals of **2**·4H$_2$O and **4**·H$_2$O were determined at room temperature. Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer with graphite monochromatic Mo-Kα (λ 0.71073) radiation. Data were collected using omega scans of 0.5° per frame and a full sphere of data were obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT[26] on all the observed reflections. Absorption corrections were applied using SADABS.[26] Structures were solved by direct methods by using the SHELXS-97 package[27] and refined using SHELXL-97.[27] Calculations were performed using the WinGX System-Version 1.80.03.[28] All hydrogen atoms were inserted in calculated positions. There were disordered molecules present in the structures of complex **6**. Since no obvious major site occupations were found for those molecules, it was not possible to model them. PLATON/SQUEEZE[29] was used to correct the data and a potential volume of 219.7 (**4**·H$_2$O) Å^3 was found with 56 electrons per unit cell worth of scattering. The electron count roughly suggests the presence of *ca.* one molecule of water for each of the unit cells. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic ones for the remaining atoms were employed.

Catalytic studies

Oxidation reactions of the alcohols were carried out in sealed cylindric Pyrex tubes under focused microwave irradiation as follows: the alcohol (5 mmol), catalysts **1**, **2** and **6** (1–100 μmol) and a 70% aqueous solution of Bu^{t}OOH (10 mmol) were introduced into the tube. This was then placed in the microwave reactor and the system was left under stirring and under irradiation (10 W) for 0.5–15 h at 80 °C.

After cooling to room temperature, 300 μL of benzaldehyde (internal standard) and 5 mL of NCMe (to extract the substrate and the organic products from the reaction mixture) were added. The obtained mixture was stirred for 10 min and then a sample (1 μL) was taken from the organic phase and analysed by GC using the internal standard method.

Conclusion

Depending on the molar ratio of pyridine used in the reaction medium, the reactions of Mn(NO$_3$)$_2$·4H$_2$O with the Schiff bases H$_3$L$^{1-3}$ in methanol at room temperature yield the dinuclear manganese(II) complexes **1–6**. In all the structures, the ligand (H$_2$L$^{1-3}$)$^-$ coordinates *via* the keto form and two ligand molecules occupy the equatorial planes. In complexes **1–3** (where pyridine was used in a 1 : 1 molar ratio), the axial positions are occupied by one pyridine molecule and one solvent molecule (water or methanol), but in **4–6** (where excess pyridine was used) each of the manganese(II) centres is axially coordinated by two pyridine molecules.

Among the six dinuclear Mn(II,II) complexes, three of them (**1**, **2** and **6**) having different coordination environments have been examined for variable temperature magnetic susceptibility measurements and have also been tested for their catalytic activity towards microwave assisted oxidation of alcohols. Magnetic analysis of these three complexes reveals that antiferromagnetic interaction is propagated between the Mn(II) centres. A yield of 81% has been found using 0.4% molar ratio of the catalyst relative to the substrate in the presence of TEMPO and in 1 M K_2CO_3 aqueous solution under mild conditions.

Hence, this work has successfully extended the use of dinuclear manganese complexes as catalyst precursors to the microwave assisted oxidation of alcohols. Tuning the ligand system or modifying the structures of the dinuclear Mn(II,II) complexes using, *e.g.*, different secondary ligands will be attempted to achieve a higher activity.

Acknowledgements

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