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Introduction

Hydrogen bonding assisted synthesis is a rapidly growing area of modern chemistry.¹ Usually, the formation of multiple hydrogen bonds, in particular resonance assisted hydrogen bonding (RAHB),² drives the reaction towards stabilized product(s). For instance, an oxygen atom of a dimethylsulfoxide (DMSO) molecule can be a bifurcate acceptor centre to create RAHB upon synthesis of Cu^{II}, Ni^{II}, Zn^{II} or Pd^{II} complexes with 1,3,5-triazapentadiene (tap) ligands.³ We believe that the formation of H-bonding between the

Halogen-bonded tris(2,4-bis(trichloromethyl)-1,3,5-triazapentadienato)-M(m) [M = Mn, Fe, Co] complexes and their catalytic activity in the peroxidative oxidation of 1-phenylethanol to acetophenone[†]

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One-pot template condensation of $CCl_3C \equiv N$ with ammonia on a metal source $[MnCl_2 \cdot 4H_2O, FeCl_3 \cdot 6H_2O$ or $Co(CH_3COO)_2 \cdot 4H_2O]$ in DMSO led to the formation of tris{2,4-bis(trichloromethyl)-1,3,5-triazapentadienato}-M(III) complexes, $[M{NH=C(CCl_3)NC(CCl_3)=NH}_3] \cdot n(CH_3)_2SO$ [M = Mn, n = 1 (1); M = Fe, n = 2 (2); M = Co, n = 2 (3)], which were characterized using elemental analysis, and IR, ESI-MS and single-crystal X-ray analysis. The role of inter- and intramolecular non-covalent halogen and hydrogen bonds in the synthesis of 1–3 is discussed. It is shown that the crystal ionic radii of the metal ions [68.5 (Co) < 69 (Fe) < 72 (Mn), pm] are related to the corresponding Cl···Cl distances [3.178 (3) > 3.155 (2) > 3.133 (1) Å]. Compounds 1–3 and the related di(triazapentadienato)-Cu(III) complex [Cu{NH=C(CCl_3)NC(CCl_3)=NH}_2] \cdot 2(CH_3)_2SO (4) act as catalyst precursors for the additive-free microwave (MW) assisted homogeneous oxidation of 1-phenylethanol with *tert*-butylhydroperoxide (TBHP), leading to the formation of acetophenone with yields up to 99% and TONs up to 5.0 × 10³ after 1 h of low power (10 W) MW irradiation.

NH moiety of the tap ligands and the DMSO molecule is one of the driving forces of this reaction.³

Non-covalent interactions between halogen atoms have also attracted much attention recently and have been demonstrated to play a prominent role in supramolecular chemistry, molecular recognition, biological systems, functional materials, etc.⁴ Halogen bonding is a rather widespread phenomenon since halogen atoms or ions can form short non-bonded contacts with electron acceptors, electron donors or be interconnected due to anisotropic charge distribution in halogen atoms. Hence, an effective polarization of halogen atoms should lead to stronger halogen bonds. One of the possible ways to reach this goal would be the introduction of a conjugated system in the nearest proximity to the halogen atom. Metallacycles provide a simple and convenient example of such charged conjugated systems;⁵ hence, they can be used to create new halogen bonds and/or to increase their energy. However, to date, not much attention has been paid to the halogen bonds in metal complexes and to the analysis of relations between parameters of such bonds and properties of the central metal ions in coordination compounds.^{3,4}

Another aspect, the study of which is still underdeveloped, concerns the application of the halogen bonds in the synthesis

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[†] Electronic supplementary information (ESI) available: Tables listing bond distances and angles, hydrogen and halogen bond geometry of compounds 1–3. CCDC 989102, 988933 and 986029. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4nj00797b

of new compounds. For instance, if, in the course of a reaction, the number and energy of the halogen bonds increase significantly, this should facilitate the formation of the products. In principle, by this way, one can influence the course of a reaction and its yield. As mentioned above, the introduction of a metallacycle in the proximity of halogen atoms can increase the anisotropy of charge distribution, thus extending the potential of the halogen atoms to form halogen bonds of higher energy.

In this study we attempt to demonstrate, by a simple but illustrative case, the significance of the halogen bonds in the synthesis of new coordination compounds. Additionally, some parameters of halogen bonds and their relationship to the properties of the metal ions will be discussed. As a model reaction, we choose the synthesis of complexes of 1,3,5-triazapentadienes (tap) with chlorinated substituents since we have significant experience with tap complexes^{3,5} and they are easy to deal with from the synthetic and crystallographic points of view. The tap complexes with halogenated groups are of particular interest due to the promotion of their volatility, chemical and thermal stability and solubility in halocarbons;^{3,5,6} these properties are important for e.g. catalytic applications.^{3a} Earlier it was demonstrated that chlorinated tap ligands can form complexes with Cu^{II},^{3b} Co^{II},^{6h} Ni^{II} , 3b,6h Mn^{II} , 6h Zn^{II} (ref. 3*a*) and Pd^{II} , 3b but Mn^{III} , Fe^{III} and Co^{III} complexes have not been synthesized and structurally characterized. Thus, it is worthwhile to expand the number of this type of complexes and perform their thorough structural analysis and application in industrially significant catalytic oxidation reactions such as the oxidation of alcohols.⁷

The oxidation of alcohols to their corresponding carbonyl compounds constitutes an important reaction in organic synthesis.⁷ When performed using non-catalytic methods, it generally produces hazardous waste.⁸ Hence, the development of catalytic oxidation procedures which involve green oxidants, shorter reaction times and/or improved selectivity is a matter of current interest.^{7–9} Recently, some of us have reported that complexes of arylhydrazones of methylene active compounds¹⁰ and tap ligands¹¹ can effectively catalyze the oxidation of 1-phenylethanol to acetophenone (Scheme 1), and we believe that the search for easy-to-synthesize and stable tap-metal catalysts for that process should be continued. Moreover, it is known that microwave irradiation (MW) in many cases provides much more efficient synthetic methods than conventional heating, and this technique has also been applied along the work.

Thus, taking in mind the above considerations, in the current work we have pursued the following aims: (i) to prepare new Mn^{III}, Fe^{III} and Co^{III} complexes with chlorinated tap ligands and demonstrate the significance of non-covalent halogen interactions in their



Scheme 1 MW-assisted oxidation of 1-phenylethanol to acetophenone. Scheme 2 Synthesis of 1-3

syntheses; (ii) to analyze some correlations between parameters of halogen bonds and properties of the central metal ions; (iii) to study the catalytic activity of the synthesized tap complexes and a related bi-tap Cu^{II} complex^{6h} in the MW-assisted homogeneous oxidation of 1-phenylethanol to acetophenone.

Results and discussion

Condensation of trichloroacetonitrile with ammonia on a metal centre

Generally, the synthesis of tap complexes of Co, Fe and Mn metal ions is not a trivial task and is achieved through rather laborious ligand pre-preparation.^{5,12} However, it is possible to prepare tap complexes with Ni and Cu metal ions using a onepot direct synthesis using nitriles as the starting materials.^{3b,5} It was also noted that Ni and Cu tap complexes from halogenated nitriles were formed with a high exothermic effect.^{3b,6h} It was supposed that this was related to the activation of the cyano carbon atom by the electron-withdrawing halogencontaining group. However, it seems that the formation of multiple hydrogen and halogen bonding in the products is more significant than the electron-withdrawing ability of a substituent. In fact, Hammett's constant σ_p^{13} of the –C(=O)CH₃ $(\sigma_p = 0.50)$ and $-C(=O)C_6H_5$ $(\sigma_p = 0.43)$ substituents is similar to that of $-CCl_3$ ($\sigma_p = 0.46$), but the direct formation of tap complexes with those substituents does not proceed and the known syntheses usually require the preliminary preparation of the tap ligands.⁵ Hence, halogen bonding can be the main driving force of the synthesis.

To explore this assumption, we performed a direct synthesis of new metal-tap complexes using trichloroacetonitrile as the starting material and Co^{III}, Fe^{III}, and Mn^{III} as the central metal ions. The known examples of tap complexes with these metal ions are very limited and include only a couple of fully characterized compounds, all of them being prepared using the presynthesized ligands.^{12b} Concerning possible applications, tap complexes of those metal ions are known catalysts for a number of oxidation reactions, in particular, of alcohols.^{5,11} Hence, a direct and simple synthesis of such a type of complexes would be of great interest.

Thus, the reaction of CCl₃CN with a metal salt [MnCl₂·4H₂O, FeCl₃·6H₂O or Co(CH₃COO)₂·4H₂O] and ammonia in DMSO afforded [M{NH=C(CCl₃)NC(CCl₃)=NH}₃]·n(CH₃)₂SO [M = Mn,



n = 1 (1); M = Fe, *n* = 2 (2); M = Co, *n* = 2 (3)] in 51–73% yield (Scheme 2). The synthesis involves an *in situ* ligand formation, in which CCl₃CN undergoes amination resulting in the formation of the tap ligand. The products 1–3 were fully characterized by elemental analysis, IR, ESI-MS and single-crystal X-ray analyses. The IR spectra of 1–3 do not exhibit the typical ν (C \equiv N) values (2100–2300 cm⁻¹ range), while new bands due to ν (NH) and ν (C \equiv N) are observed at 3246–3441 and 1576–1696 cm⁻¹, respectively. The ESI-MS spectra confirm the existence of monoprotonated molecular ion peaks at 970, 971 and 974 for 1, 2 and 3, respectively. The elemental analyses are consistent with the proposed formulations, which are also supported by X-ray crystallography.

In the molecular structures of **1–3** (Fig. 1), the central metal atom is located in a markedly distorted octahedral geometry environment and bonded by six nitrogen atoms from the three tap ligands. The M–N distances in **1–3** are in the range of 1.892(4)–1.966(5) Å (Table S1 in the ESI†) and increase with the growth of the ionic radius of the metal ion [68.5 (Co) < 69 (Fe) < 72 pm (Mn)]. A similar trend was found for the M–N bond distance in the chlorinated tap ligands.^{3b} The N–M–N bite angles in the sixmembered planar metallacycles are in the range of 84.7(2)–98.7(2)° and are close to those in related compounds.³ Each bidentate tap ligand forms a six-membered metallacycle MNCNCN where, for the N=C–N–C=N moiety, a short–long–long–short

pattern of C–N bond lengths can be seen. For example, for complex **1** the N(1)–C(2), C(2)–N(3), N(3)–C(4) and C(4)–N(5) distances are 1.288(8), 1.366(8), 1.350(8) and 1.257(8) Å, respectively (Table S1, ESI \dagger).

Due to the stabilization of the formed products 1–3 by hydrogen (Table S2, ESI[†]) and halogen bonds (Table S3, ESI[†]), a highly exothermic effect is observed in the reaction. An extensive interlinkage takes place *via* intermolecular hydrogen bonding between the hydrogen atoms of two imino (C==NH) groups and the oxygen atom of dimethylsulfoxide, giving rise to six-membered H-bond supported cycles (Fig. 1 and Scheme 3). The average C==NH···O=S(CH₃)₂ distances of the hydrogen bonds in 1–3 fall in the 2.15–2.64 Å range (Table S2, ESI[†]), which is consistent with a strong hydrogen bonding. In all the structures, the oxygen atoms of DMSO molecules play an acceptor role giving bifurcated or three-centred hydrogen bond systems (Fig. 1 and Scheme 3). The NH···O distances become longer in the three-centred hydrogen bonds than in the bifurcated ones (Fig. 1).

Extensive halogen bonding between the molecules of complexes is also observed, with -CCl₃ groups acting as both nucleophiles and electrophiles, which successfully drive the formation of a multitude of self-assembled architectures (Fig. 2 and Table S3, ESI†). Thus, the crystal packings of **1–3** are similar and reveal infinite strands of the complexes assembled



Fig. 1 Molecular structures of 1-3 (H atoms of DMSO molecules are omitted for clarity). N(1)–C(2) and C(4)–N(5), N(1)–C(2) and C(4)–N(5), N(8)–C(9) and C(11)–N(12) are 1.288(8) and 1.257(8), 1.295(4) and 1.287(4), 1.268(6) and 1.283(6) Å, respectively, while C(2)–N(3) and N(3)–C(4), C(2)–N(3) and N(3)–C(4), C(2)–N(3) and N(3)–C(4), C(9)–N(10) and N(10)–C(11) are of 1.366(8) and 1.350(8), 1.326(5) and 1.321(4), 1.331(6) and 1.329(6).



Scheme 3 Bifurcated or three-centred hydrogen bond systems in 1-3



Fig. 2 Cl...Cl interactions in 1–3; DMSO molecules are omitted for clarity.

by the Cl···Cl intermolecular interactions between chlorine atoms (Fig. 2). Additionally, intermolecular N···Cl interactions are observed between the N3 and the Cl atom of $-\text{CCl}_3$ groups at a distance of 3.221(6)-3.225(6) Å (Table S3, ESI†). Thus, cooperation of the six-membered hydrogen bonding system and Cl···Cl interactions (Tables S2 and S3, ESI†) leads to 3D supramolecular architectures in all structures. The Cl···Cl distance is shorter in the case of 1 compared to that in 2 or 3. An increase of the ionic radius of the metal ion appears to correspond to a decrease in the Cl···Cl distance (Fig. 3), but no clear linear relationship ($r^2 = 0.846$) was found between the mentioned parameters. Although further examples have to be obtained to confirm the trend, these results are indicative that the polarization of the halogen atom depends on the metal ion involved in the close-by metallacycle.

Microwave-assisted catalytic peroxidative oxidation of 1-phenylethanol

Complexes 1-3 (Scheme 2) and the known¹¹ bis(2,4-bis-(trichloromethyl)-1,3,5-triazapentadienato)- $Cu(\pi)$ (4) were tested as catalyst precursors for the additive-free microwave (MW) assisted homogeneous oxidation of secondary alcohols [1-phenyl-ethanol (chosen as the model substrate), cyclohexanol, 2-hexanol and 3-hexanol] to the corresponding ketones by aqueous *tert*-butylhydroperoxide (Bu^tOOH, TBHP) or hydrogen peroxide under low power (10 W) irradiation, without an added solvent (Scheme 1). Selected results are summarized in Table 1.

Under typical additive-free conditions all the compounds exhibited catalytic activity for the above reactions, leading to

Fig. 3 Plot of the ionic radius of metal ions *versus* the shortest Cl \cdots Cl distances for **1–3**.

yields (based on the alcohol) of acetophenone up to 99% after 1 h of irradiation (Table 1 and Fig. 4). The catalyst precursors 2–4 were highly active (TOFs up to 5.5×10^3 h⁻¹ for 3). The best acetophenone yields were obtained in the presence of the Co(m)

3 (99%, entry 5, Table 1) and Cu(II) 4 (97%, entry 7, Table 1) complexes. The activities of the Fe(III) 2 (87%, entry 3, Table 1) and the Mn(III) 1 (34%, entry 1, Table 1) complexes are lower, but still significant. Moreover, a high selectivity towards the formation of acetophenone was observed in these MW-assisted transformations, since no traces of by-products were detected by GC-MS analysis of the final reaction mixtures (only the unreacted alcohol was found, apart from the ketone).

Complexes 1–4 were also tested towards the oxidation of other secondary alcohols, namely cyclohexanol and the linear 2- and 3-hexanols. The ketones are the only oxidation products obtained (Table 1). The aliphatic alcohols are less reactive than the benzylic derivative, 1-phenylethanol, leading under the same reaction conditions to moderate yields in the 22–68% range (Table 1), as reported in other cases.^{7e,10,11,14,15} Moreover, the efficiency of oxidation of those linear aliphatic alcohols is not significantly affected by the position (2 or 3) of the OH

Entry	Catalyst precursor	Substrate	Catalyst/substrate molar ratio (%)	Reaction time (h)	Yield ^b (%)	TON^{c} (TOF (h^{-1}))
1	1	1 Phonylothanol	0.02	1	22 5	$1.68 \times 10^3 (1.68 \times 10^3)$
d^{1}	1	1-Pitenyietitanoi	0.02	1	33.5	$1.08 \times 10 (1.08 \times 10)$
2	2		0.02	1	26.9	$4.22 \times 10^3 (4.22 \times 10^3)$
Λ^d	2		0.02	1	10.0	$4.32 \times 10 (4.32 \times 10)$
- <u>+</u> 5	2		0.02	1	00.1	$4.96 \times 10^3 (4.96 \times 10^3)$
5 6 ^d	3		0.02	1	24.2	$4.90 \times 10^{-} (4.90 \times 10^{-})$ $1.21 \times 10^{3} (1.21 \times 10^{3})$
7	3		0.02	1	07.4	$1.21 \times 10^{-} (1.21 \times 10^{-})$ $4.97 \times 10^{3} (4.97 \times 10^{3})$
od	4		0.02	1	21.0	$4.87 \times 10^{-} (4.87 \times 10^{-})$ $1.05 \times 10^{3} (1.05 \times 10^{3})$
0	4		0.02	1	21.0 54.6	$1.03 \times 10^{-} (1.03 \times 10^{-})$ $2.73 \times 10^{3} (5.47 \times 10^{3})$
9 10	3		0.02	0.3	26.1	$2.73 \times 10^{-} (3.47 \times 10^{-})$ $1.20 \times 10^{3} (5.21 \times 10^{3})$
10	3		0.02	0.25	20.1	$1.30 \times 10^{-} (3.21 \times 10^{-})$ $2.01 \times 10^{2} (8.03 \times 10^{2})$
11	3		0.2	0.23	40.2	$2.01 \times 10^{2} (6.03 \times 10^{2})$
12	3		0.2	0.3	30.7 40.7	$2.64 \times 10 (3.67 \times 10)$
13 14 ⁰	3		2	0.25	40.7	20(81)
14	3		0.02	1	41.1	$2.06 \times 10 (2.06 \times 10)$
15 1 <i>c</i> f				1	/.1	 228 (228)
10 ^g	3		0.02	1	4.8	238 (238)
170	3		0.02	1	5.3	263 (263)
18	1	Cyclohexanol	0.02	1	26.5	$1.33 imes 10^3 (1.33 imes 10^3)$
19	2		0.02	1	58.5	$2.93 \times 10^3 (2.93 \times 10^3)$
20	3		0.02	1	67.9	$3.40 \times 10^3 (3.40 \times 10^3)$
21	4		0.02	1	68.4	$3.42 imes 10^3 (3.42 imes 10^3)$
22	1	2-Hexanol	0.02	1	22.3	$1.12 imes 10^3 (1.12 imes 10^3)$
23	2		0.02	1	67.0	$3.35 \times 10^3 (3.35 \times 10^3)$
24	3		0.02	1	61.1	$3.06 \times 10^3 (3.06 \times 10^3)$
25	4		0.02	1	35.7	$3.40 imes 10^3 \left(3.40 imes 10^3 ight)$
26	1	2-Hevanol	0.02	1	24.7	$1.70 \times 10^3 (1.70 \times 10^3)$
20	2	5-110,20101	0.02	1	24.7 66.4	$1.79 \times 10^{-} (1.79 \times 10^{-})$ $2.22 \times 10^{3} (2.22 \times 10^{3})$
27	2		0.02	1	59.2	$3.32 \times 10^{-} (3.32 \times 10^{-})$ $2.96 \times 10^{3} (2.96 \times 10^{3})$
20	3		0.02	1	20.5	$2.90 \times 10^{-} (2.90 \times 10^{-})$ $1.52 \times 10^{3} (1.53 \times 10^{3})$
29	4		0.02	1	30.3	$1.55 \times 10 (1.55 \times 10)$
30	MnCl ₂ ·4H ₂ O	1-Phenylethanol	0.02	1	12.3	615 (615)
31	FeCl ₃ ⋅6H ₂ O		0.02	1	45.8	$2.29 imes 10^3~(2.29 imes 10^3)$
32	Co(MeCO ₂) ₂ ·4H ₂ O		0.02	1	39.3	$1.97 imes 10^3 \ (1.97 imes 10^3)$
33	$Cu(NO_3)_2$		0.02	1	33.4	$1.67 imes 10^3 (1.67 imes 10^3)$
34	CoCl ₃ ·6H ₂ O		0.02	1	27.7	$1.39 imes 10^3 \ (1.39 imes 10^3)$
35	CuCl ₂		0.02	1	17.2	860 (860)

^{*a*} Reaction conditions unless stated otherwise: 5 mmol of substrate, 1–100 μ mol (0.02–2 mol% *vs.* substrate) of 1–4, 10 mmol of TBHP (2 eq., 70% in H₂O), 80 °C, 15–60 min reaction time, MW irradiation (10 W power). ^{*b*} Moles of acetophenone per 100 moles of 1-phenylethanol. ^{*c*} Turnover number = number of moles of product per mol of the catalyst precursor; TOF = TON per hour (values in brackets). ^{*d*} 10 mmol of H₂O₂ (30% aqueous solution) instead of TBHP. ^{*e*} 5 mmol of TBHP. ^{*f*} In the presence of Ph₂NH (10 mmol). ^{*g*} In the presence of CBrCl₃ (10 mmol).



Fig. 4 Effect of the reaction time and oxidant (TBHP or H_2O_2) on the yield for the oxidation of 1-phenylethanol to acetophenone catalyzed by **1–4** (' means that the oxidant is hydrogen peroxide).

group in the aliphatic chain, as attested by the similar yields of 2- and 3-hexanones (compare *e.g.*, entries 23 and 27, Table 1).

The MW assisted reaction proceeds rapidly under the low irradiation power of 10 W used (an increasing of the power up to 25 W did not show a significant yield enhancement) and is highly effective even with very low catalyst amounts. For example, in the presence of 1 μ mol (0.02 mol% vs. substrate) of 3 a fair yield of acetophenone (55%, entry 5, Table 1) was already achieved in 30 min, whereas an almost quantitative yield was obtained in 1 h (entry 3, Table 1 and Fig. 4) under MW irradiation. An increase in the catalyst amount from 1 µmol (0.02 mol% vs. substrate) to 10 µmol (0.2 mol% vs. substrate) results in a yield enhancement for shorter reaction times (from 26% to 40%, 15 min, Table 1, entries 10 and 11, respectively) but is not significant after 30 min of irradiation (compare entries 9 and 12, Table 1). Moreover, beyond 10 µmol of the catalyst, the yield remained almost unchanged, even at 15 min irradiation, leading to the expected TON lowering (entry 13, Table 1). Blank tests (in the absence of any catalyst precursor) were performed under common reaction conditions and no significant conversion was observed (7%, entry 10, Table 1).

Microwave irradiation (10 W) provides a more efficient synthetic method than conventional heating, thus allowing the attainment of similar yields in shorter times, as observed in other cases.^{7e,11,14,15} For example, in the presence of 3, 99% yield of acetophenone was reached after a 1 h reaction under the MW irradiation, while the reaction under conventional heating (oil bath) gave only 13% yield. It takes 28 h (instead of 1 h) to achieve the 99% acetophenone yield using the latter heating method.

Related Cu(II) compounds with 1,3,5-triazapentadiene ligands tested under the same reaction conditions were found¹¹ to achieve quantitative yields in half of the reaction time needed by the present complexes with chlorinated tap ligands, but the former required a higher amount (0.2 mol% vs. substrate) of the catalyst. Nevertheless, even the less efficient compound of this study, the Mn(III) complex **1**, is much more efficient than other known manganese complexes with hydrazone Schiff bases^{15a} (acetophenone yield of 7%, TON of 27, after 1 h of 10 W irradiation; 0.1 mol% vs. substrate) or a dinuclear μ -chloridobridged manganese species^{15b} (acetophenone yield of 5%, TON of 238, after 3 h of 10 W irradiation; 0.02 mol% vs. substrate).

The relevance of the tap ligands to the catalytic activity of the obtained compounds is shown by the much lower catalytic performances of the corresponding metal salts in the oxidation of the model substrate used (yields in the 12–46% range, entries 30–35, Table 1) under the same reaction conditions.

The cheaper and environmentally friendly hydrogen peroxide (30% aqueous solution) is not as efficient an oxidant as TBHP, as attested by the marked yield lowering from *e.g.*, 99% to 24% (3) (entries 5 and 6, respectively, Table 1), in accordance with the expected decomposition of H_2O_2 under the used reaction conditions (80 °C). Furthermore, the use of an equimolar amount of oxidant to substrate leads to a drastic decrease of the acetophenone yield (compare entries 5 and 14, Table 1).

Carrying out the reaction in water (up to 2 mL) does not markedly change the yield of acetophenone either using TBHP or H₂O₂ under the same conditions. Hence, for example, in the presence of **3** and under the conditions of entry 5 of Table 1, the 99% acetophenone yield achieved without any added solvent decreased to 93% in water. A similar behaviour was previously reported^{14*a*} for the Cu(II) complex [Cu(H₂O)(HL)]· H₂O [H₂L = (*E*)-2-(((1-hydroxynaphthalen-2-yl)methylene)amino)benzenesulfonic acid]. However, for some Mn systems,¹⁵ the use of water as a solvent led to a considerable reduction of the yield of the oxidized product.

The addition to the reaction mixture of Ph₂NH or CBrCl₃, well-known oxygen- or carbon-radical traps, respectively,¹⁶ strongly hampers the catalytic activity (entries 16 and 17, Table 1). This suggests the generation of oxygen and carbon radicals in the reaction, which are trapped by those radical scavengers. The mechanism may involve *e.g.*, ^{*t*}BuO• and ^{*t*}BuOO• radicals produced in the metal (M) promoted decomposition of TBHP¹⁷ according to the following equations.

$$\mathbf{M}^{n+} + {}^{t}\mathbf{B}\mathbf{u}\mathbf{OOH} \rightarrow \mathbf{M}^{(n-1)+} + {}^{t}\mathbf{B}\mathbf{u}\mathbf{OO}^{\bullet} + \mathbf{H}^{+}$$
(1)

 $\mathbf{M}^{(n-1)^{+}} + {}^{t}\mathbf{B}\mathbf{u}\mathbf{O}\mathbf{O}\mathbf{H} \rightarrow \mathbf{M}^{n+}-\mathbf{O}\mathbf{H} + {}^{t}\mathbf{B}\mathbf{u}\mathbf{O}^{\bullet}$ (2)

 $M^{n+}-OH + {}^{t}BuOOH \rightarrow M^{n+}-OO - {}^{t}Bu + H_2O$ (3)

 ${}^{t}BuO^{\bullet} + RR'CHOH \rightarrow {}^{t}BuOH + RR'C^{\bullet}-OH$ (4)

 ${}^{t}BuOO^{\bullet} + RR'CHOH \rightarrow {}^{t}BuOOH + RR'C^{\bullet}-OH$ (5)

 $M^{n+}-OO^{-t}Bu + RR'C^{\bullet}-OH \rightarrow RR'C = O + {}^{t}BuOOH + M^{(n-1)+}$ (6)

It may also proceed *via* the coordination of the alcohol substrate to an active site of the catalyst, and its deprotonation to form the alkoxide ligand, followed by a metal-centred dehydrogenation.¹⁷

Conclusions

In the current study we have prepared a series of structurally similar Mn(m), Fe(m) and Co(m) complexes with chlorinated tap ligands, which were characterized using elemental analysis, IR,

ESI-MS and single-crystal X-ray analyses. The role of hydrogen and halogen bonds in the synthesis of these complexes was recognized, while a trend between the ionic radius of the metal ion and the $\text{Cl} \cdots \text{Cl}$ distance (which is related to the strength of the halogen bonding) was found. The obtained trend can potentially be used to tune various properties of complexes with halogenated ligands such as acidity, photoluminescence, coordination ability, among others, which are known to be dependent on halogen bonding.⁴⁻⁶

In this study, we have also successfully explored the catalytic activity of four metal complexes (1–4) with the chlorinated tap ligand towards MW-assisted oxidation of secondary alcohols (1-phenylethanol) with TBHP or H_2O_2 , in additive-free systems. It was demonstrated that the Fe, Co and Cu complexes 2–4 act as efficient and selective homogeneous catalyst precursors for the above reaction, which is fast, selective, requires a very small amount of catalyst precursor and proceeds in the absence of any additional solvent or additives, which are features of significance towards the development of a "green" catalytic process.

Experimental

Materials and methods

Infrared spectra (4000–400 cm⁻¹) were recorded on a Vertex 70 (Bruker) instrument in KBr pellets. Carbon, hydrogen, and nitrogen elemental analyses were done using a Perkin Elmer 2400 CHN Elemental Analyzer. Electrospray mass spectra were run using an ion-trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer) equipped with an electrospray (ESI) ion source. For electrospray ionization, the drying gas and flow rate were optimized according to the particular sample with 35 p.s.i. nebulizer pressure. Scanning was performed from m/z 100 to 1200 in methanol solution. The compounds were observed in the positive mode (capillary voltage = 80 to 105 V). The catalytic tests under MW irradiation were performed in a focused microwave Anton Paar Monowave 300 reactor (10 W), using a 10 mL capacity reaction tube with 13 mm internal diameter, fitted with a rotational system and an IR temperature detector. Gas chromatographic (GC) measurements were carried out using a FISONS Instruments GC 8000 series gas chromatograph with a DB-624 (I&W) capillary column (FID detector) and the Jasco-Borwin v.1.50 software. The temperature of injection was 240 °C. The initial temperature was maintained at 120 °C for 1 min, then raised 10 $^\circ C$ min^{-1} to 200 $^\circ C$ and held at this temperature for 1 min. Helium was used as the carrier gas. GC-MS analyses were performed using a Perkin Elmer Clarus 600 C instrument (He as the carrier gas). The ionization voltage was 70 eV. Gas chromatography was conducted in the temperatureprogramming mode, using a SGE BPX5 column (30 m \times 0.25 mm \times 0.25 µm). Reaction products were identified by comparison of their retention times with known reference compounds, and by comparing their mass spectra to fragmentation patterns obtained from the NIST spectral library stored in the computer software of the mass spectrometer.

Syntheses of the complexes

To a mixture of 1.6 mL (11 mmol) trichloroacetonitrile and 2.5 mL (1 M) NH₄OH in 20 mL DMSO, 1 mL water solution of 1.1 mmol metal salt [MnCl₂·4H₂O, FeCl₃·6H₂O or Co(CH₃COO)₂·4H₂O] was added, and the system was stirred for 10 min under ambient conditions giving a dark red (1), red (2) or light red (3) precipitate of the respective product which was filtered off and dried in air. Crystals suitable for X-ray structural analysis were obtained by recrystallization of 1–3 from DMSO.

[Mn{NH=C(CCl₃)NC(CCl₃)=NH₃]·(CH₃)₂SO (1): yield 73%; IR (KBr, selected bands, cm⁻¹): 3375 and 3246 ν (N–H), 1696 ν (C=N), 1617 δ (NH). ESI-MS (in methanol): *m*/*z* 970 [M-DMSO + H]⁺. Elemental analysis calculated (%) for C₁₄H₁₂Cl₁₈MnN₉OS₃, *M* = 1047.46: C 16.05, H 1.15, N 12.03; found: C 15.88, H 1.33, N 11.79.

[Fe{NH=C(CCl₃)NC(CCl₃)=NH}₃]·2(CH₃)₂SO (2): yield 65%; IR (KBr, selected bands, cm⁻¹): 3441, 3334 and 3255 ν (N-H), 1576 ν (C=N), 1508 δ (NH). ESI-MS (in methanol): *m*/*z* 971 [M-2DMSO + H]⁺. Elemental analysis calculated (%) for C₁₆H₁₈Cl₁₈FeN₉O₂S₂, *M* = 1126.50: C 17.06, H 1.61, N 11.19; found: C 17.02, H 1.91, N 11.03.

[Co{NH=C(CCl₃)NC(CCl₃)=NH}₃]·2(CH₃)₂SO (3): yield 51%; IR (KBr, selected bands, cm⁻¹): 3335 ν (N-H), 1596 ν (C=N), 1528 δ (NH). ESI-MS (in methanol): *m*/*z* 974 [M-2DMSO + H]⁺. Elemental analysis calculated (%) for C₁₆H₁₈Cl₁₈CON₉O₂S₂, *M* = 1129.59: C 17.01, H 1.61, N 11.16; found: C 16.89, H 1.70, N 10.95.

X-ray structure determination

The diffraction experiments were carried out on a Bruker SMART APEX-II CCD diffractometer. The program SHELXTL^{18a} was used for collecting frames of data, indexing reflections and for the determination of the lattice parameters, SAINTP^{18b} for integration of the intensity of reflections and scaling, SADABS^{18c} for absorption correction, and SHELXTL^{18a} for the space group and structure determination, least-square refinements on F_2 . Crystallographic and selected structural details are listed in Table 2.

General procedure for the peroxidative oxidation of 1-phenylethanol

In a typical experiment, the alcohol substrate (5.00 mmol), TBHP (70% aqueous solution, 10.0 mmol) and the catalyst precursor **1–4** (1–100 µmol, 0.02–2 mol% *vs.* substrate) were introduced into a cylindrical Pyrex tube, which was then placed in the focused microwave reactor. The system was stirred and irradiated (10 W) for 15 min–1 h at 80 °C. After the reaction, the mixture was allowed to cool down 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 during 10 min and then a sample (1 µL) was taken from the organic phase and analysed by GC (or GC-MS) using the internal standard method. Blank tests indicate that only 7% of acetophenone is generated in a metal-free system (Table 1).

Table 2 Crystallographic data and structure refinement details for 1-3

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	1	2	3
Empirical formula	C14H12Cl18MnN9OS	C ₁₆ H ₁₈ Cl ₁₈ FeN ₉ O ₂ S ₂	C ₁₆ H ₁₈ Cl ₁₈ CoN ₉ O ₂ S ₂
fw	1047.43	1126.48	1129.54
λ (Å)	0.71073	0.71073	0.71073
Temperature (K)	100(2)	296(2)	296(2)
Cryst. syst.	Triclinic	Triclinic	Triclinic
Space group	P1	$P\bar{1}$	$P\bar{1}$
a (Å)	14.257(2)	10.0591(4)	10.171(3)
b (Å)	16.101(2)	13.5688(5)	13.499(4)
<i>c</i> (Å)	19.044(3)	16.6349(6)	16.468(5)
α(°)	104.391(2)	79.4670(10)	79.309(6)
β (°)	102.766(2)	76.0640(10)	76.007(6)
γ(°)	111.467(2)	75.1320(10)	74.967(6)
$V(Å^3)$	3697.2(9)	2112.09(14)	2100.6(10)
Ζ	4	2	2
Density	1.882	1.771	1.786
GOOF	1.002	1.005	1.004
$R_1^{a} (I \ge 2\sigma)$	0.0722	0.0749	0.0770
$wR_2^{b} (I \ge 2\sigma)$	0.1074	0.1718	0.1981
^{<i>a</i>} $R_1 = \Sigma F_0 - F_c / \Sigma F_0 $. ^{<i>b</i>} w	$R_{2} = \left[\Sigma[w(F_{o}^{2} - F_{c}^{2})^{2}]/\Sigma[w(F_{o}^{2})^{2}]\right]^{1/2}.$		

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