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Author: Oksana V. Nesterova Dmytro S. Nesterov Agnieszka Krogul M. Fátima C. Guedes da Silva Armando J.L. Pombeiro

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Synthesis, crystal structures and catalytic activity of Cu(II) and Mn(III) Schiff base complexes: influence of additives on the oxidation catalysis of cyclohexane and 1-phenylehanol

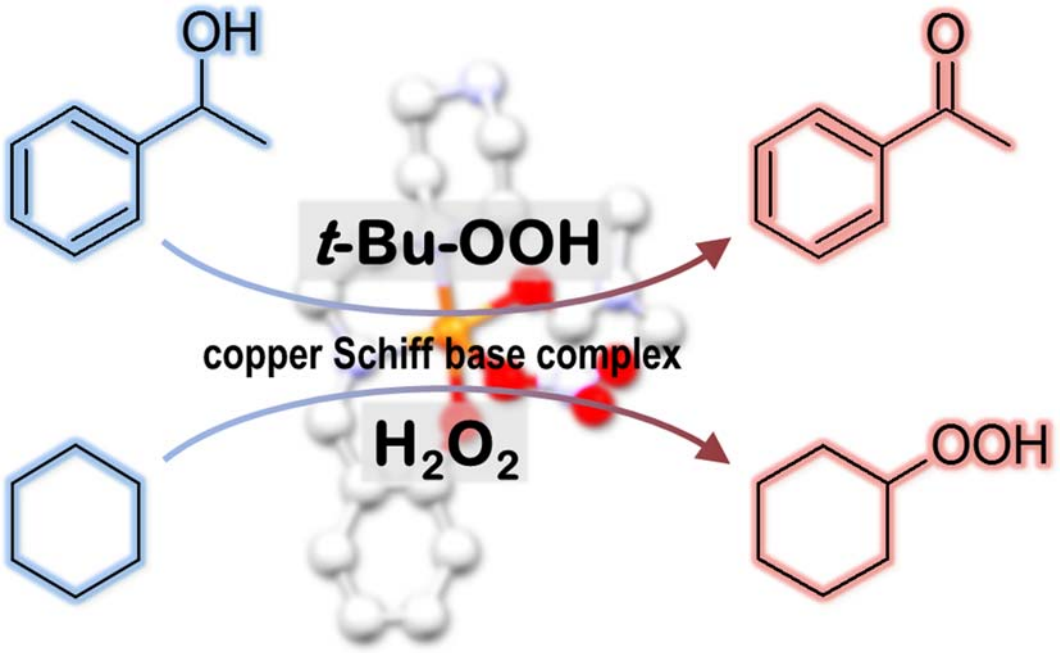
Oksana V. Nesterova,[a]Dmytro S. Nesterov,[a] Agnieszka Krogul,[b] M. Fátima C. Guedes da Silva[a]* and Armando J. L. Pombeiro[a]**

[a] Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av.Rovisco Pais, 1049-001 Lisboa, Portugal; e-mails: dmytro.nesterov@tecnico.ulisboa.pt; fatima.guedes@tecnico.ulisboa.pt; pombeiro@tecnico.ulisboa.pt

[b] Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093, Warsaw, Poland.

Dedicated to Prof. Georgiy B. Shul'pin on the occasion of his 70th birthday and as a recognition for his scientific achievements.

Graphical Abstract



Highlights

- Oxidation of cyclohexane with H_2O_2 catalysed by copper and manganese complexes.
- Pronounced promoting effect of pyridine.
- Direct GCMS observation of cyclohexyl hydroperoxide as a main reaction product.
- The formation of chlorocyclohexane in the presence of HCl promoter.
- Solvent-free oxidation of phenylethanol with *t*-BuOOH.

Abstract

The complexes of copper [Cu(κ*ONN*'-HL)(NO_3)(DMF)](NO_3)·H_2O (**1**) and[Cu(κ*ONN*'-HL)Cl_2]·½DMSO (**2**), and of manganese [Mn(κ*ON*-HL)$_2Cl_2$]Cl (**3**) and [Mn(κ*ON*-HL)$_2$(NO_3)$_2$](NO_3)·H_2O (**4**) were synthesized by reactions of the respective chloride or nitrate salt with a non-aqueous solutions of the Schiff base aminoalcohol HL (product of condensation of salicylic aldehyde and aminoethylpiperazine) and characterized by X-ray diffraction analysis. The catalytic investigations disclosed a prominent activity of the copper compounds **1** and **2** towards oxidation of cyclohexane with hydrogen peroxide in the presence of various promoters (nitric, hydrochloric, oxalic acids and pyridine), under mild conditions. The unusual promoting effect of pyridine on the catalytic activity of the copper catalysts allowed to achieve yields up to 21% based on cyclohexane. Chromatographic studies revealed that cyclohexyl hydroperoxide is a main reaction product and chlorocyclohexane (in the presence of HCl as promoter) was also detected, suggesting a free radical reaction pathway with hydroxyl radicals as attacking species. Complexes **1** and **2** act also as catalysts in the oxidation of 1-phenylethanol with *tert*-butylhydroperoxide, showing acetophenone yields up to 62% and TON (turnover numbers) up to 620 in the presence of the K_2CO_3 promoter.

Keywords: alkane oxidation; alcohol oxidation; hydrogen peroxide; alkyl radical; metal complex **catalysis.**

1. Introduction

Complexes of copper and manganese attract special attention, namely due to their ability to show phenomena such as molecular magnetism[1] and magnetic refrigerating,[2] bioactivity,[3]*etc*. Furthermore, copper and manganese are found in active centres of many bioenzymes,[4, 5] for example in superoxide dismutase (dismutation of superoxide),[6]catalase (decomposition of hydrogen peroxide),[7]particulate methane monooxygenase(methane oxidation)[8]or photosystem II(water photooxidation).[9, 10]This encourages the study of those metals for simple catalytic models of enzymatic systems, in attempting to approach their activity and explain their mechanisms of action. Complexes of copper and manganese with polydentate amine and aminoalcohol ligands are also recognized as catalysts in oxidative catalysis, particularly in C–H functionalization of various substrates.[11, 12]The activation of alkanes and alcohols under mild conditions is a principal step towards their conversion into valuable chemicals,[13-15]providing a strong motivation for further investigation of N,O-donor copper and manganese complexes.

Schiff bases are useful tools in the construction of novel ligand systems by means of *in situ* condensation of a variety of readily available aldehydes and amines.[16-18] Recently, we described the iron complex $[Fe^{III}(HL)Cl_2(DMF)]Cl{\cdot}DMF$ with the Schiff base ligand HL formed from salicylic aldehyde and aminoethylpiperazine.[19] That complex exhibited an excellent catalytic activity in cyclohexane oxidation with H_2O_2 in the presence of nitric acid as a promoter.[19]The presence of the promoter was crucial, and only a weak activity was found in its absence or in the presence of another promoting agent(acetic acid). The importance of an acid promoter (nitric acid) was also observed for the heterometallic complex $[Co_4Fe_2O(L^1)_8]{\cdot}4DMF{\cdot}H_2O$ with a Schiff base ligand (H_2L^1 = salicylidene-2-ethanolamine), which is an exceptionally active catalyst in the mild oxidation of cycloalkanes with hydrogen peroxide in the presence of that acid,[20] as well as for other Schiff base and aminoalcohol catalysts.[21-25]Based on those results, we have now synthesized four novel complexes of copper and manganese with the ligand HL and tested their catalytic activity in two radical reactions, oxidation of cyclohexane and 1-phenylethanol in the presence of various promoting agents.

2. Experimental

All chemicals were of reagent grade and used as received. All experiments were carried out in air. Elemental analyses for CHNS were provided by the Microanalytical Service of the Instituto Superior Técnico. Infrared spectra (4000–400 cm^{-1}) were recorded using a BX-FT IR "Perkin Elmer" instrument in KBr pellets.

*2.1 Synthesis of [Cu(κONN'-HL)(NO_3)(DMF)](NO_3)·H_2O (**1**):*

Salicylaldehyde (0.53 mL, 5 mmol) and 1-(2-aminoethyl)piperazine (0.66 mL, 5 mmol) were dissolved in DMF (20 mL), forming a light-yellow solution which was magnetically stirred at 50–60 °C (30 min). Then, a solution of $Cu(NO_3)_2·2.5H_2O$ (1.16 g, 5 mmol) in 5 mL of DMF was added dropwise and the resulting green mixture was magnetically stirred for 30 min. Green crystals suitable for X-ray crystallographic study were formed in one month after addition of ^{i}PrOH and Et_2O. Yield: 0.85 g, 34%. Anal. calc. for $C_{16}H_{28}CuN_6O_9$ (M = 511.98): C, 37.5; N, 16.4; H, 5.5%. Found: C, 37.8; N, 16.5; H, 5.3%. The compound is sparingly soluble in DMSO, DMF, water and CH_3CN.

*2.2 Synthesis of [Cu(κONN'-HL)Cl_2]·½DMSO(**2**):*

Salicylaldehyde (0.53 mL, 5 mmol) and 1-(2-aminoethyl)piperazine (0.66 mL, 5 mmol) were dissolved in DMSO (20 mL), forming a light-yellow solution which was magnetically stirred at 50–60 °C (30 min). Then, a solution of $CuCl_2·2H_2O$ (1.16 g, 5 mmol) in 5 mL of DMSO was added dropwise and the resulting green mixture was magnetically stirred for 30 min. Green crystals suitable for X-ray crystallographic study were formed in one day after standing at room temperature. Yield: 0.44 g, 10%. Anal. calc. for $C_{28}H_{44}Cl_4Cu_2N_6O_3S$ (M = 813.63): C, 41.3; N, 10.3; H, 5.5%. Found: C, 38.5; N, 8.5; H, 5.7% (the difference with calculated values is due to the presence of DMSO molecules, which were not accounted by the X-ray analysis). The compound is sparingly soluble in DMSO, DMF, water and CH_3CN.

*2.3 Synthesis of [Mn(κON-HL)$_2$$Cl_2$]Cl (**3**):*

Salicylaldehyde (0.53 mL, 5 mmol) and 1-(2-aminoethyl)piperazine (0.66 mL, 5 mmol) were dissolved in CH_3OH (25 mL), forming a light-yellow solution which was magnetically stirred at 50–60 °C (30 min). Then, a solution of $MnCl_2 \cdot 4H_2O$ (0.98 g, 5 mmol) in 5 mL of CH_3OH was added dropwise and the resulting yellow-brown mixture was magnetically stirred for 30 min. Dark-brown crystals suitable for X-ray crystallographic study were formed in three days after addition of ^{i}PrOH. Yield: 1.15 g, 37%. Anal. calc. for $C_{26}H_{38}Cl_3MnN_6O_2$ (M = 627.91): C, 49.7; N, 13.4; H, 6.1%. Found: C, 50.1; N, 13.9; H, 5.6%. The compound is sparingly soluble in DMSO, DMF and CH_3CN.

*2.4 Synthesis of $[Mn(\kappa ON\text{-}HL)_2(NO_3)_2](NO_3)\cdot H_2O$ (**4**):*

Salicylaldehyde (0.27 mL, 2.5 mmol) and 1-(2-aminoethyl)piperazine (0.33 mL, 2.5 mmol) were dissolved in CH_3OH (20 mL), forming a light-yellow solution which was magnetically stirred at 50–60 °C (30 min). Then, a solution of $Mn(NO_3)_2 \cdot 4H_2O$ (0.63 g, 2.5 mmol) in 5 mL of CH_3OH was added dropwise and the resulting green-brown mixture was magnetically stirred for 30 min. Brown-violet crystals suitable for X-ray crystallographic study were formed in one month after addition of ^{i}PrOH and Et_2O. Yield: 0.78 g, 44%. Anal. calc. for $C_{26}H_{40}MnN_9O_{12}$ (M = 725.61): C, 43.0; N, 17.4; H, 5.6%. Found: C, 42.6; N, 17.2; H, 5.8%. The compound is sparingly soluble in DMSO, DMF and CH_3CN.

2.5 Crystallography

The X-ray diffraction data (Table 1) were collected using a Bruker AXS KAPPA APEX II diffractometer with graphite-monochromated Mo-Kα radiation. Data were collected using omega scans of 0.5° per frame, and a full sphere of data was 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.[27] The structures of were solved by direct methods using SIR-97[28] and refined with SHELXL-2014/7.[29] Calculations were performed using the WinGX System-Version 2014.1.[30]

For all the non-hydrogen atoms, least square refinements with anisotropic thermal motion parameters were employed and isotropic for the remaining atoms. The hydrogen atoms bonded to carbon were included at geometrically calculated positions and refined using a riding model. $U_{iso}(H)$ were defined as

$1.2U_{eq}$ of the parent carbon atoms for phenyl and methylene residues and $1.5U_{eq}$ of the parent carbon atoms for the methyl groups. The hydrogen atoms of the ammonium groups were not located from the difference Fourier map and thus were included in the final refinement at positions calculated from the geometry of the molecules, with distances and angles restrains. There were disordered molecules in the structure of **2** which could not be modelled and the electron density was removed by using Platon/Squeeze routine. The total number of electrons (289) and void volume (772 $Å^3$) suggest the presence of six DMSO molecules (42 electrons and a volume of 129 $Å^3$ per molecule) which were not included in the final refinement. CCDC 1474857 (**1**), 1474858 (**3**), 1474859 (**4**), 1474860 (**2a**) and 1474861(**2**) contain the supplementary crystallographic data for this paper.

2.6 Catalytic oxidation of cyclohexane

To5 μmol of solid catalyst weighed into the reaction flask, 4.4 mLCH_3CN, 50 μmol of promoter (HCl and HNO_3 were used as 37 and 65% aqueous solutions, respectively; solid oxalic acid was weighted in the same flask prior addition of solvent), 0.5 mL of CH_3NO_2stock solution (internal standard; 1 mL of CH_3NO_2 mixed with 9 mL of CH_3CN), 108 μL (1 mmol) of cyclohexane and 0.28 mL (5 mmol; 50% aqueous) of H_2O_2were added in this order at 50 °C under vigorous stirring (CAUTION: the combination of air or molecular oxygen and H_2O_2 with organic compounds at elevated temperatures may be explosive!). Aliquots (ca. 0.5 mL) of reaction mixture were transferred, upon cooling, into a vial containing an excess (ca. 150 mg) of solid Ph_3P. A Perkin-Elmer Clarus500 gas chromatograph with a BP-20 capillary column (SGE,30 m × 0.32 mm × 25 μm) and a Perkin-Elmer Clarus 600 gas chromatograph, equipped with a Perkin-Elmer Clarus 600 C mass-spectrometer (electron impact), with a BPX5 capillary column (SGE, the same dimensions) and helium carrier gas were used for quantitative analyses of the reaction mixtures.

2.7 Catalytic oxidation of 1-phenylethanol

In a typical experiment, 1-phenylethanol (5.00 mmol), TBHP (70% aqueous solution, 10.0 mmol) and catalyst precursor **1**–**4** (2.5 – 5 μmol, 0.05 – 0.1 mol% vs. substrate) were introduced to a cylindrical glass tube, which was then placed in a hot oil bath. The system was stirred for 2 h at 80 °C. After the

reaction was completed, the mixture was allowed to cool down to room temperature. 300 μL of benzaldehyde (internal standard) and 5 mL of acetonitrile (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 (or GC–MS) using the internal standard method.

3. Results and discussion

3.1 Synthesis, spectroscopic analysis

The complexes **1**–**4** were obtained using a two steps synthetic strategy(Scheme 1): 1) *in situ* formation of a Schiff base ligand and 2) its complexation reaction with a metal precursor. The ligand HL was obtained by *in situ* condensation of the salicylaldehyde and 1-(2-aminoethyl)piperazine. The choosing synthetic method is widely used as an efficient tool for the preparation of Schiff base containing coordination complexes. Applying of such an approach allows to make the immediate utilization of the Schiff base ligand formed, since its formation is a reversible process and its elaboration can be problematic due to the low yields and laborious separation procedures. The interaction of metal chlorides or nitrates with a non-aqueous solutions of HL using a molar ratio of MX_n : HL = 1 : 1, resulted in green or brown solutions (for Cu and Mn, respectively) obtained at the end of the reactions. The reactions were initiated and brought to completion by heating and stirring in open air. Microcrystals of the complexes **1**–**4** were formed in *ca.*1 month after successive addition of ^{i}PrOH and diethyl ether into the resulting solutions (**1** and **4**) or after standing at room temperature within one day (**2**) or in three days after addition of ^{i}PrOH (**3**).

The IR spectra of **1**–**4** in the 4000–400 cm^{-1} range confirmed the presence of the Schiff base ligand. The broad medium intensity bands in the 3400–3550 cm^{-1} region were attributed to ν(O–H) vibrations of HL. The very strong bands at 1643 (**2**), 1623 (**3**) and 1617 cm^{-1} (**4**) were assigned to *ν*(C=N) stretching vibrations of the Schiff bases and the peak at 1637 (**1**) was attributed to the overlapped ν(C=N) and ν(CO) vibrations of both Schiff base ligand and DMF. The presence of the nitrate ligand in **1** and **4** can be identified by the strong ν(NO)absorption peaks at 1384 cm^{-1} in the spectra of both compounds. The presence of DMSO solvate molecule in **2** can be identified by the peak at 1017 cm^{-1} that corresponds to the ν(S=O) vibration.

3.2 Crystal structures

The asymmetric unit of **1** consists of one $[Cu(\kappa ONN'\text{-}HL)(NO_3)(DMF)]^+$ cation, one NO_3^- anion and a water molecule, which joined into supramolecular one-dimensional chains assisted by hydrogen bonds (Figs. 1, right and S1).The Schiff base HL in **1** shows a tridentate chelation mode with the binding atoms occupying three of the basal metal coordination sites; the remaining equatorial position is engaged with the O_{DMF} atom and the axial location with the $O_{nitrate}$ thus rendering the metal cation with a distorted square-pyramidal (τ_5 = 0.24)[31] O_3N_2coordination environment (Fig. 1, left). The Cu–O bond lengths assume values of 1.9066(15), 1.9560(15) and 2.455(2) Å, the larger values involving the DMF and nitrate O-atoms, in this order (Table S1). Concerning the Cu–N bond distances, the one *trans* to the $O_{fenolate}$ is larger than that opposite to O_{DMF} (2.0954(16) against 1.9259(17) Å) thus revealing a larger *trans* effect of the anionic group as compared to the neutral one. The O–Cu–N_{trans} angles are 163.25(7) and 177.61(7)º. The nearest Cu···Cu non-bonded separations within the supramolecular chain are 7.159(1) Å.

The asymmetric unit of **2** contains two crystallographically independent molecules of $[Cu(\kappa ONN'\text{-}HL)Cl_2]$, revealing close geometrical parameters (Table S2, Fig. 2, left), and one DMSO molecule. The copper atoms in **2** have distorted square-pyramidal coordination environments (τ_5 = 0.28 and 0.31)[31] with ON_2Cl_2 donor sets formed by the donor atoms of the Schiff base and two chloride anions. The basal Cu–X (X = O, N, Cl) bond lengths in **2** range from 1.926(12) to 2.255(5) Å, while the apical ones are of 2.719(6) Å (Cu1–Cl1) and 2.806(6) Å (Cu2–Cl3). The O(Cl)–Cu–N_{trans} angles assume values between 157.2(6) to 175.7(5)º. The molecules of **2** are packed into 2D supramolecular layers by means of strong hydrogen bonding between the nitrogen atoms of HL and the chloride anions (Fig. 2, right). The nearest Cu···Cu distance in **2** is of 4.817(3) Å.

An interesting feature of complex **2** is the ability to recrystallize from the perfluoropolyetheroil "Fomblin Y", to give complex $[Cu(\kappa ONN'\text{-}HL)Cl_2]\cdot 2.5DMSO$ (**2a**) (Table S2, Fig. 3). The effect has been observed during the single crystal X-ray experiment (this oil is commonly used to fix the crystal in the loop), where new crystals grew on the sample plate after 24h. While the original formulae of the molecule of **2** remains unchanged, the crystal structure undergo drastic changes in the geometrical parameters (Table S2), in the cell symmetry ($P2_12_12_1$ in **2** but $P\bar{1}$ in **2a**) and in the number of crystallization DMSO molecules. The metal complexes in **2a** are associated into 2D layers by means of N–H···Cl and N–H···O_{HL} interactions (Figs. S2 and S3) and ultimately give rise to a 3D network upon

longer range contacts with the DMSO molecules. The closest Cu···Cu distance in the structure of **2a** (6.518(2) Å) is larger than that in **2** (see above). Since the perfluoropolyetheroil is known as a highly inert compound and a poor solvent, the present effect of recrystallization of the coordination compound with the "classical" N,O-donor ligands is a rare effect with deserves further investigation.

The manganese complexes **3** and **4** contain the HL ligand coordinated in a N,O-chelating fashion (Figs. 4 and 5), with the coordination polyhedrons around the Mn centres in both structures adopting $O_2N_2Cl_2$ (in **3**) or O_4N_2 (in **4**) octahedral geometries. The X–Mn–X_{trans} (X = O, N, Cl) angles are of 180.0º (Tables S3 and S4) and the compounds crystallized with uncoordinated chloride (in **3**) or nitrate (in **4**) anions. The molecules of **3** and of **4** are packed into a 3D supramolecular network by means of H-bonding interactions (Figs. S4 and S5).The nearest Mn···Mn distance is of 8.704(0) (in **3**) and 8.397(19) Å (in **4**).

A striking feature of the structure of **4** concern the relative orientation of the nitrate ligands in the two crystallographically independent molecules present in the structure, since in one of them (that of Mn2) the O-atoms establish short range contact interactions with the delocalized π-systems of the $MnOC_3N$ metallacycles [N20–O23···*centroid* 2.936(6) Å].

3.3 Catalytic oxidation of cyclohexane

Complexes **1**–**4** were studied as catalysts in the oxidation of cyclohexane with H_2O_2 in acetonitrile, in the presence of various co-catalysts (promoters). Cycloalkanes, particularly cyclohexane, are useful model substrates towards establishing the C–H functionalization activity of novel catalytic systems. The C–H bond dissociation energy of cyclohexane (97 kcal/mol)[32] is high enough to prevent its catalyst-free oxidation with organic peroxides under mild conditions and low concentrations. Further, the mild oxidation of cyclohexane typically gives just two main products, cyclohexanol and cyclohexanone, which can be easily quantified, thus facilitating the catalytic studies. Promoting agents can play a complex role in the oxidation process. Strong protic acids (*e.g.* nitric, hydrochloric, trifluoroacetic acids) may create an unsaturated coordination environment around the metal cation upon ligand protonation and also hamper undesired decomposition of hydrogen peroxide (catalase-like

activity).[19-21, 24, 33]Carboxylic acids (*e.g.* acetic, oxalic, pyrazinecarboxylic acids) can serve as agents stabilizing transition states of metal catalysts.[34-36] Basic promoters (*e.g.* triethylamine, pyridine) are known to interact with metal catalysts converting them into active species.[37-40]

It has been shown that the catalytic activity of copper compounds (such as **1** and **2**) in the mild cyclohexane oxidation is typically enhanced by the presence of a protic acid as a promoter,[24, 25, 41] while the activity of manganese compounds (such as **3** and **4**) is sensitive to carboxylic acids.[35, 42-44]Thus, we decided to study the influence of these typical acid promoters, as well as of a basic one (pyridine, for comparative purpose), on the catalytic activity of complexes **1**–**4**(Scheme 2).

The yields of products after 3 h reaction time are shown in the Table 2. The copper complexes**1** and **2**act as catalysts in all the cases, except of oxalic acid, where no products were detected even at trace levels. Despite having very close structures, **1** and **2** reveal different catalytic activities upon treating with the same promoting agents. The initial reaction rates $W_0$of cyclohexane oxidation with HNO_3 promoter were estimated as 9×10^{-7} and 3.1×10^{-5} and M $s^{-1}$for **1** and **2**, respectively. Interestingly, the reaction rate exhibited by the complex **2** after decay of the initial activity becomes close to that observed for **1** (Fig. 6*a*).In contrast to nitric acid, the hydrochloric acid promoter leads to very close yields (Table 2) and reaction rates (7.7×10^{-6} M s^{-1}) for **1** and **2**.No alkane oxidation products were obtained in the absence of the catalyst.

The accumulation dependences are also similar (Fig. 6*b*), pointing out that the catalytic behaviours of **1** and **2**in the presence of HCl are identical. Pyridine provides the highest yields (Table 2) and reaction rates ($W_0 > 2.6 \times 10^{-5}$ M s^{-1}) for complexes **1** and **2** within the range of conditions studied. As it can be seen (Fig. 6*c*), the catalytic system based on the complex **2** reaches a plateau upon 20 min after the reaction starts, with no further change in the yield, whereas the compound **1** does not lose its activity until 2 h reaction time.

The manganese complexes **3** and **4** were found to be almost inactive under all conditions studied. Pyridine was the best promoting agent, but even in its presence the yields of products based on the cyclohexane did not exceed 0.3% (Table 2). The initial reaction rate W_0 (calculated for complex **3**) was found to be just 6×10^{-7} M s^{-1}, which, among the **1** – **4** systems with detectable activity, is the lowest one. In the presence of promoters other than pyridine, the complexes **3** and **4** were found to be

completely inactive: no even traces of products were detected, even employing mass-spectral analysis of reaction products.

The reaction mechanisms are believed to proceed *via* formation of free carbon-centred radicals as main C–H bond attacking species. Such pathway is expected[45] for transition metal complexes interacting with a large excess (*e.g.*, 1000 equiv.) of hydrogen peroxide. The principal processes of this mechanism are as follows. Reduction of H_2O_2 by a $[M^n]$ leads to the formation of a hydroxyl radical:

$$[M^n] + H_2O_2 \rightarrow [M^{n+1}] + HO^- + HO\bullet$$

The latter is a strong hydrogen abstracting agent, able to split even cyclohexane C–H bond:

$$HO\bullet + R–H \rightarrow R\bullet + H_2O$$

The alkyl radical reacts with dioxygen to form alkyl peroxide radical, which then transforms into alkyl hydroperoxide[45, 46] via a set of complex reactions:

$$R\bullet + O_2 \rightarrow ROO\bullet$$

$$ROO\bullet + [M^n] \rightarrow [M^{n+1}] + ROO^-$$

$$ROO^- + H^+ \rightarrow ROOH$$

$$[M^{n+1}] + H_2O_2 \rightarrow [M^n] + H^+ + HOO\bullet$$

$$ROO\bullet + HOO\bullet \rightarrow ROOH + O_2$$

The main product from this mechanism is alkyl hydroperoxide (ROOH), not alcohol or ketone. No alkyl hydroperoxide is formed when the alkane is oxidized by high-valent metal-oxo species without participation of long-living alkyl radicals (oxygen rebound and related mechanisms).[47, 48]

Cyclohexyl hydroperoxide is a relatively unstable compound and its decomposition route depends on reaction and/or analytical conditions.[45] While in a typical catalytic mixture it gradually decomposes to cyclohexanol and cyclohexanone, an attempt to analyse the reaction samples using conventional gas chromatography (GC) technique may lead to other products due to catalytic decomposition of hydroperoxide in the hot injector and/or GC column. Bearing this in mind, reaction samples are typically quenched with a strong reducing agent (Ph_3P) before injection into the GC, according to the following reaction:

$ROOH + Ph_3P \rightarrow ROH + Ph_3P{=}O$

This method, developed by Shul'pin,[45]quantitatively transforms organo-hydroperoxides to the respective alcohols and in this way allows a correct estimate of products, avoiding spontaneous decomposition of RCOOH. Also, the comparison of chromatograms taken before and after addition of Ph_3P may confirm the presence or absence of ROOH in the reaction mixture.[45] For a selected catalytic system (complex **2** and nitric acid), the concentrations of cyclohexanone and cyclohexanol were measured before and after addition of Ph_3P, giving A/K (alcohol/ketone) ratios of 1 and 19, respectively. The large prevalence of cyclohexanol after addition of Ph_3P is a strong evidence for the presence of cyclohexyl hydroperoxide.

It has been shown that cyclohexyl hydroperoxide can be directly detected[49] using proper conditions of GC measurements (particularly, clean injector and non-polar capillary column) and preferably employing GC-MS techniques.[50-52] Hence, all samples of catalytic reactions taken at 1h reaction time were subjected for GC-MS tests (see experimental part for details) before and after addition of Ph_3P. All active tests revealed the presence of cyclohexyl hydroperoxide, according to mass-spectrometry. The example chromatograms of the cyclohexane oxidation catalysed by complex **1** in the presence of HCl is shown at Fig. 7.

The large peak of ROOH completely disappears after addition of Ph_3P to the reaction sample. Formation of cyclohexyl hydroperoxide is a direct evidence of a free-radical reaction mechanism, as described above, where the main attacking species is hydroxyl radical. Finally, careful investigation of the chromatograms disclosed the presence of chlorinated products, namely derivatives of cyclohexane and acetonitrile (Fig. 6*b*).

The presence of hydroxyl radicals as the main attacking species was additionally confirmed by a bond selectivity test. Oxidation of methylcyclohexane revealed the formation of the products (alcohols and ketones) with the normalized 1° : 2° : 3° ratios shown in Table 3 (Fig. S6). The bond selectivities exhibited by the catalysts **1**–**4** are close to those observed for other catalytic systems known to generate hydroxyl radicals (Table 3). For the copper catalysts **1** and **2** the ratio between primary and secondary oxygenated C–H bonds was surprisingly low (1° : 2° = 1 : 2) (Table 3), while this parameter typically ranges from 1 : 3 to 1 : 10. The overall yields of products for **1** and **2** were estimated as 15.2 and 9.9%, respectively, after 1 hour reaction time. This is slightly lower than those observed for oxidation of cyclohexane (18.3 and 15.1%, respectively, Fig. 6c).The chromatograms recorded before addition of

PPh_3 to the reaction samples revealed a group of peaks (Fig. S7, 13.9–14.2 mins retention time) which disappear after the addition of the solid PPh_3. The mass-spectra of this group show peaks up to 155 *m/z* (Fig. S8). This *m/z* value is higher than that expected (130 *m/z*.) for the methylcyclohexyl hydroperoxide molecular ion. Therefore, the above group of peaks possibly belongs to derivatives formed upon decomposition of alkyl hydroperoxides in the GC injector or column. No methylcyclohexyl hydroperoxide was detected, in contrast to the cyclohexyl hydroperoxide (Fig. 7).

Pyridine was found to be the most efficient promoter in cyclohexane oxidation, giving the best yields in combination with copper complexes (Table 2). The promoting effect of pyridine has been recognized in the acceleration of formation of catalytically active species[39] and in hydrogen atom transfer mediating.[55] Pyridine may also compete with the alkane substrate in the reaction with the hydroxyl radical,[40, 56] in this way influencing the reaction pathway. The presence of pyridine is somewhat related to Gif chemistry,[46, 57] where metal (iron or copper) catalysts are used in this solvent or its mixture with acetic acid. However, in our case pyridine is applied as a promoter, being in a small concentration compared to that of the solvent. Further, no pyridine derivatives were detected among the reaction products, suggesting that it does not serve as a hydroxyl radical acceptor under the conditions used (probably due to 20 fold excess of CyH). Pyridine (and species incorporating it, such as bipyridine) are known to form stable coordination compounds with copper. Hence, in our case pyridine presumably acts (i) by coordinating the metal centre, (ii) facilitating proton-transfer steps, e.g. in the conversion of hydrogen peroxide into the hydroxyl radical[53, 58], and/or (iii) favouring the oxidation of Cu(I) to Cu(II), as observed for Fe/Py catalytic systems.[46]In the case of pyridine, the difference between the activities of complexes **1** and **2** can conceivably be explained by higher lability of the monodentate chloride anions in **2** compared to the nitrate anion in **1** (Scheme 1). It is known that nitrate anion is able to bind copper ions in a bidentate-chelate mode.[59] The DMF molecule in **1** may decoordinate in solution, with rearrangement of nitrate to form a chelate, thus interfering with the coordination of hydrogen peroxide and/or of pyridine promoter, resulting in a lower reaction rate (Fig. 6c).

In the presence of hydrochloric acid promoter both copper complexes **1** and **2** revealed similar activities (Table 2, Fig. 6b), suggesting the substitution of nitrate anion in the coordination sphere of **1** for chloride anions. The opposite replacement (of chloride in **2** by nitrate), when the reaction is performed with HNO_3 promoter, is slower and may explain the initial period of high reaction rate of the **2**/HNO_3 system (Fig. 6a, curve 2). The complete inhibition of the catalytic activity in the presence of

oxalic acid can be associated to its irreversible coordination to metal centres. Formation of binuclear species, where oxalic acid serves as a bridge, is also a possibility. In both cases no sufficient vacant positions remain in the coordination spheres, suppressing the catalytic activity.

The formation of R–Cl products (chlorocyclohexane, Fig. 6*b*) resembles the peroxidative halogenation process, catalysed by chloroperoxidases[60] and model metal complexes[61]:

$H_2O_2 + Cl^- + H^+ + R–H \rightarrow R–Cl + 2H_2O$

The mechanism of such a process may proceed via metal-promoted oxidation by $H_2O_2$of chloride to HOCl with the subsequent halogenation of the hydrocarbon[60, 62]:

$H_2O_2 + Cl^- + H^+ \rightarrow HOCl + H_2O$

$HOCl + R–H \rightarrow R–Cl + H_2O$

Alternatively, the metal-catalysed oxidation of chloride with H_2O_2 in acidic medium can lead to the chloro radical[63] which, upon reaction with the alkyl radical, forms the halogenated product (chlorocyclohexane).

3.4 Catalytic oxidation of 1-phenylethanol

Complexes **1**–**4** were also tested as catalysts for the peroxidative oxidation of 1-phenylethanol to acetophenone using aqueous *tert*-butylhydroperoxide (TBHP) as oxidizing agent (Scheme 3), in a solvent-free medium under typical conditions (see Table 4, footnote *a*). The choice of this model reaction was justified by its importance in chemical industry.[64]

The effects of various factors (presence of additives, amount of catalyst and reaction temperature) on the yield of acetophenone and selectivity of the catalyst were investigated (the results are summarized in Table 4, and Fig. 9). The reaction carried out under typical additive-free conditions and in the presence of a low amount of catalyst (0.05 mol% *vs*. substrate) leads to a rather low (10–20%) yield of acetophenone and TON (moles of product per mol of catalyst precursor) of 200-500 for all the investigated complexes (entries 1, 9, 17, 25 in Table 4).

The next series of reactions were performed in the presence of the catalyst (**1**–**4**) and different additives (Fig. 9*a*). The addition of either TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy, a free radical) or NHPI (precursor of phthalimido-*N*-oxyl radical) increases the yield and TON for **1** and **3** (entries 2, 5, 18,21 in Table 4), whereas no significant influence of these additives is observed for **2** and **4** (entries 10, 13, 26,29 in Table 4).The presence of HNO_3 hampers the reaction (entries 4, 12, 20,28 in Table 4). Such inhibitory effect is observed for all investigated complexes and similar observation can be found in the literature.[65-68] In contrast, the addition of K_2CO_3 significantly increases the reaction rate. Such results are in agreement with the previously recognized promoting effect of basic additives.[69, 70]

The effect of the amount of catalyst was also studied (Fig. 9*b*, Table 4). A two-fold increase of this amount causes almost at wo-fold increase of the acetophenone yield in the case of **1** (entry 6 in Table 4); however, if a double amount of **2**–**4** is used, the yield remains almost unchanged, leading to the corresponding TON decrease (compare *e.g.* entries 19 and 22 in Table 4). Blank tests in the absence of the catalyst precursor, performed under the typical reaction conditions, reveal very low yields (entries 33–35 in Table 4). Moreover, the reaction strongly depends on the temperature (Fig. 8) and we observe a different influence of temperature on the activity of Mn(III)-based catalyst (**3** and **4**) comparing to the Cu(II)-based ones (**1** and **2**). The highest catalytic activity of Mn(III) complexes was noticed when the reaction was conducted at 80 °C, whereas the activity of the Cu(II) complexes increases with increasing temperature and the highest yield and TON values were obtained at 100 °C (Figs. 8, 9*c*). The lower yield in the case of the Mn(III) complexes **3** and **4** can be related to their decomposition under the used reaction conditions in contrast to **1** and **2** which are conceivably more stable.

Attempts to perform the oxidation of 1-phenylethanol at 50 °C resulted in a marked drop in the yield of acetophenone relative to that obtained at 80 °C (for each complex, Fig. 8). Furthermore, we see that the nature of the coordinated anion has prominent influence on the activity of the catalyst. Probably, the behaviours of nitrate and chloride anions should be similar to those for cyclohexane oxidation (see above), with chloride anions being more labile. The oxidation of 1-phenylethanol at 80 °C without any additives, in the presence of the same molar amount of **1**, led to a much lower yield of acetophenone than that obtained for **2** (entries 1 and 9 in Table 4) and the same relation is observed for Mn(III)-based catalyst **3** and **4** (compare entries 17 and 25 in Table 4). The dependences of the yield on the temperature for complexes **1** and **2** are similar to those reported for aminoalcohol complexes of

copper.[71] In all experiments, a high selectivity towards the formation of the ketone was found since no traces of by-products were detected by GC and GC–MS analyses of the final reaction mixtures (only the unreacted alcohol and the ketone product were found).

4. Conclusions

We have synthesized novel coordination compounds of Cu(II) and Mn(III) with a polydentate Schiff base ligand, which were characterized by single-crystal X-ray diffraction. One of the copper compounds (**2**) was found to exhibit a rare effect of spontaneous recrystallization from the Fomblin perfluoropolyether oil. Complexes **1**–**4** were tested as catalysts in the reaction of mild oxidation of cyclohexane with hydrogen peroxide in the presence of acidic (nitric, hydrochloric and oxalic acids) and basic (pyridine) promoters. It was found that the most active systems comprise the copper complexes **1** and **2** with pyridine as promoter, showing high yields of products (cyclohexanol and cyclohexanone) up to 21 % based on the substrate. To date, pyridine was known to promote the catalytic activity of osmium and vanadium complexes,[39, 55] while copper-based systems typically benefit from an acidic promoter.[25] Herein we demonstrate that pyridine can be successfully applied as a promoter in the catalytic oxidation of cyclohexane with hydrogen peroxide catalysed by copper species.

In all the active systems the presence of cyclohexyl hydroperoxide was detected by GC-MS techniques, pointing out a free radical pathway with the hydroxyl radical as the main C–H attacking species. In addition, chlorocyclohexane was also detected (in the reaction performed in the presence of HCl), what constitutes a rare observation and is of significance for achieving alkane chlorination.

In the studies of 1-phenylethanol oxidation with TBHP (*tert*-butylhydroperoxide) the highest activity was exhibited by the copper complex **1**, whereas the other compound of copper (**2**), being also active, showed a slightly lower activity. These copper complexes can also be applied as effective catalyst precursors in the solvent-free oxidation of 1-phenylethanol.However, the coordination compounds of manganese (**3** and **4**) were found to possess a lower activity under all the conditions studied.

Acknowledgements

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Supplementary material

Selected bond lengths and angles for crystal structures of **1**–**4** (Tables S1–S4), description and figures of their supramolecular structures, chromatograms and mass-spectra of the reaction products in the methylcyclohexane oxidation.

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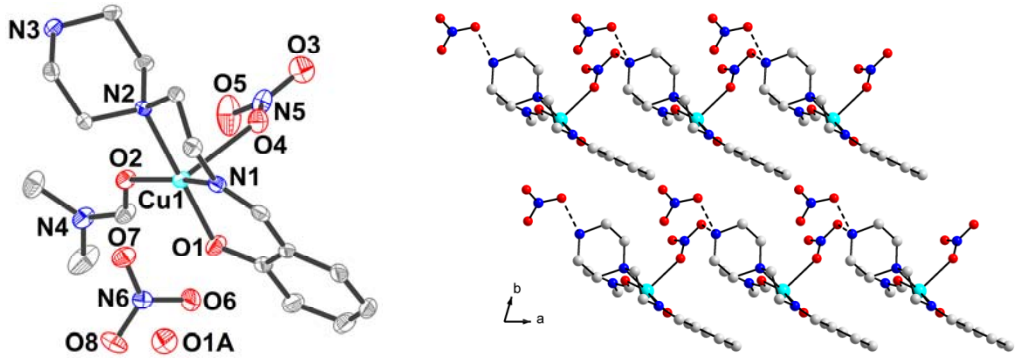


Figure 1. Left: the crystal structure of **1**with 50% probability thermal ellipsoids,showing the atom numbering. H atoms are omitted for clarity. Right: The packing of the H-bonded chains in 1 viewed down the c axis.

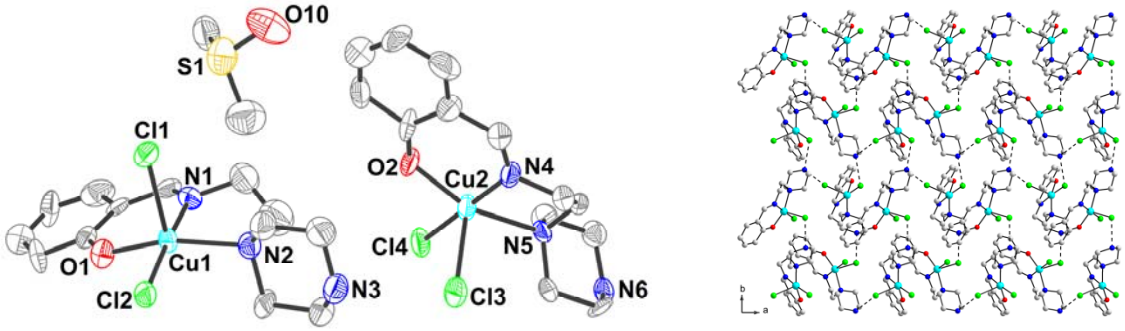


Figure 2. Left: the crystal structure of **2** with 50% probability thermal ellipsoids, showing the atom numbering. H atoms are omitted for clarity. Right: a fragment of the supramolecular 2D layer in **2**, viewed down the crystallographic c axis. DMSO molecules are omitted for clarity.

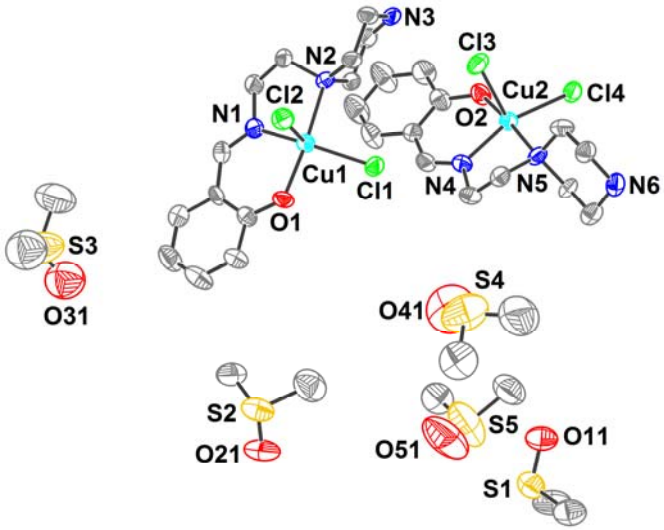


Figure 3.The crystal structure of **2a**with 50% probability thermal ellipsoids, showing the atom numbering. H atoms are omitted for clarity.

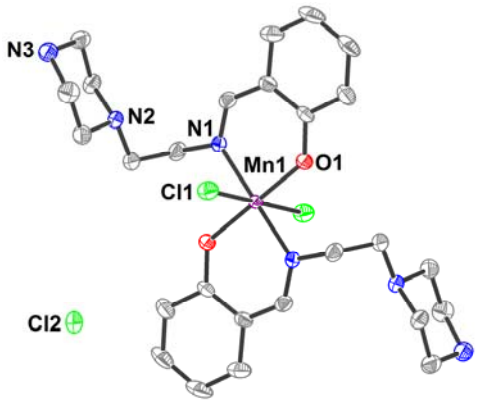


Figure 4.The crystal structure of **3**with 50% probability thermal ellipsoids, showing the atom numbering.

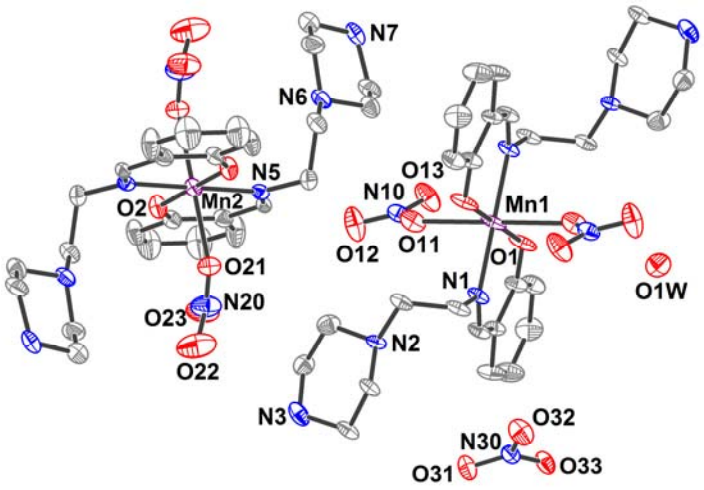
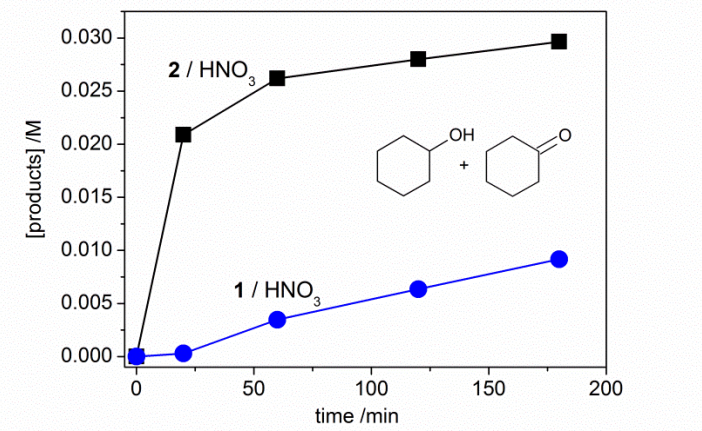
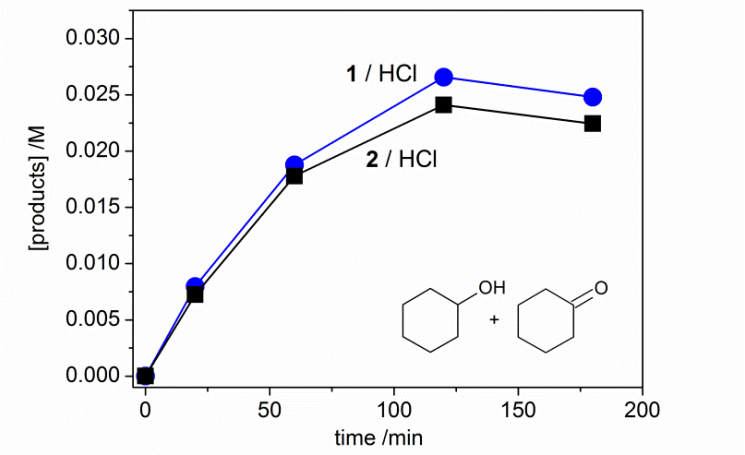


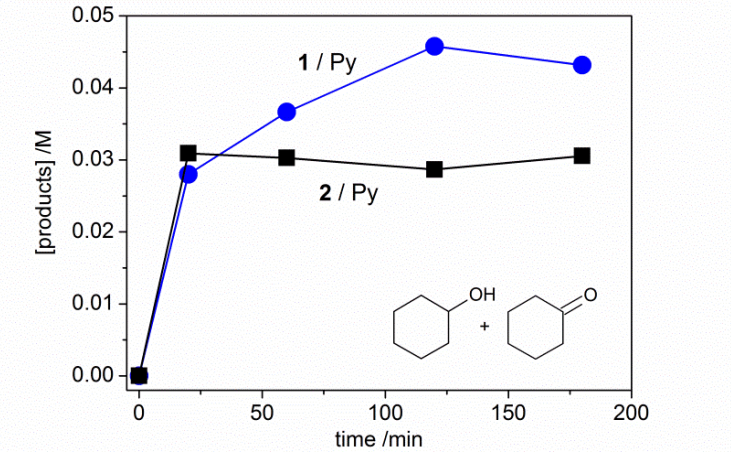
Figure 5.The crystal structure of **4**with 30% probability thermal ellipsoids, showing the atom numbering.



a



b



c

Figure 6. Accumulations of oxygenates (sums of cyclohexanol and cyclohexanone) with the time in cyclohexane (0.2 M) oxidation with H_2O_2 (1 M), catalysed by complexes **1** or **2** (1×10^{-3} M) in the presence of HNO_3 (0.01 M) (*a*), HCl (0.01 M) (*b*) and pyridine (0.01 M) (*c*), in acetonitrile (total volume of the reaction solution was 5 mL) at 50 °C.

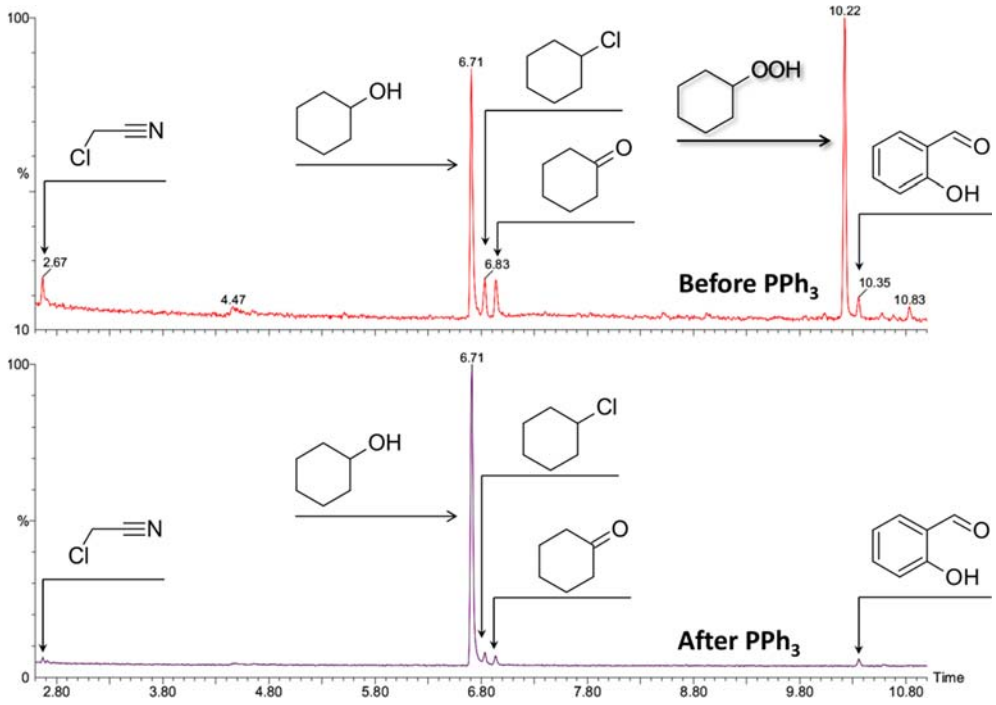


Figure 7.Fragments of the chromatograms (see Fig. 6*b* caption for reaction conditions), showing the main reaction products (recorded before and after addition of solid Ph_3P, top and bottom, respectively).The large peak of cyclohexyl hydroperoxide, seen at 10.22 min (top chromatogram), completely disappears after addition of Ph_3P (bottom chromatogram). The weak peak of salicylic aldehyde appears from the decomposition of the ligand H_2L in the GC injector.

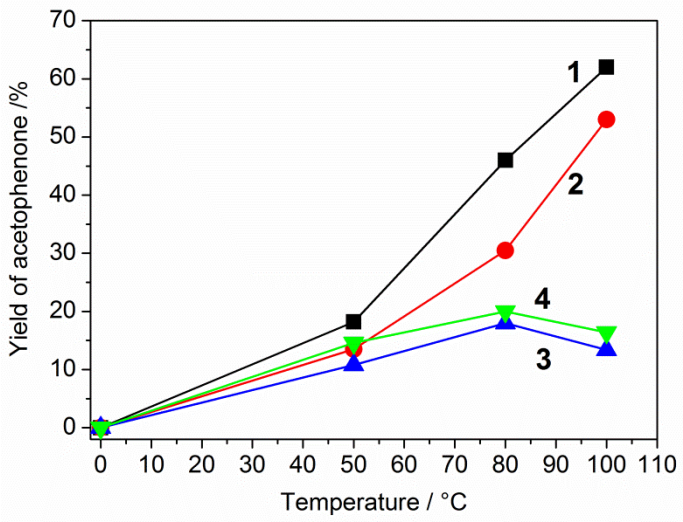
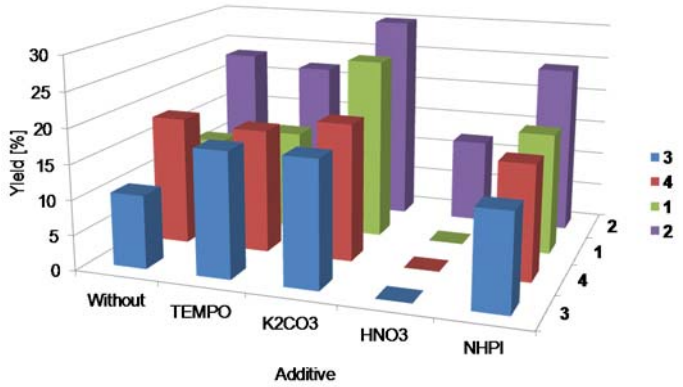
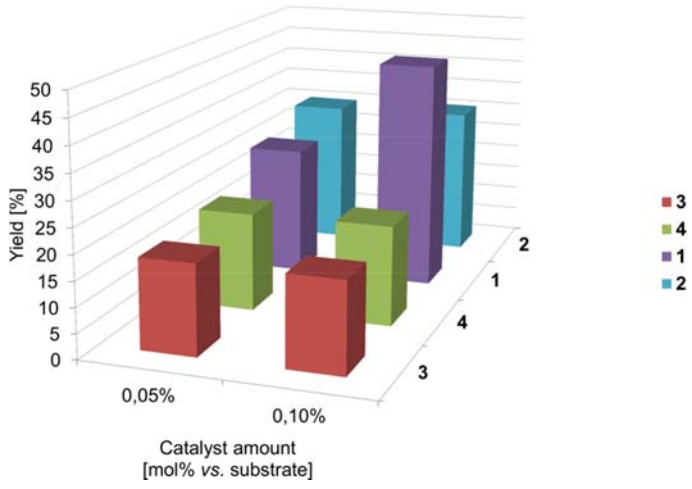


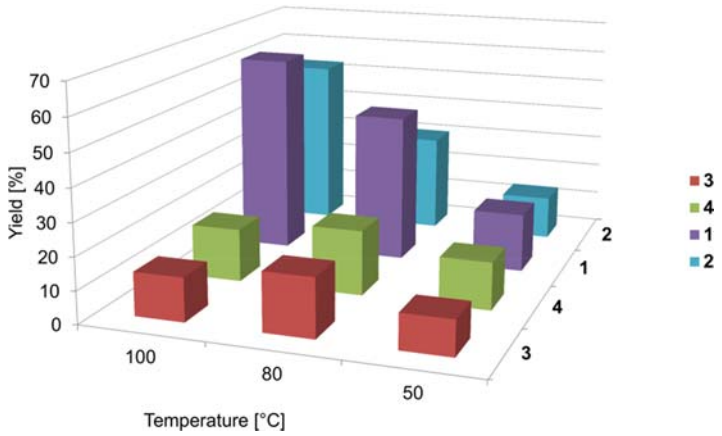
Figure 8. Dependences of the acetophenone yield on the reaction temperature, in the presence of K_2CO_3 additive.



a

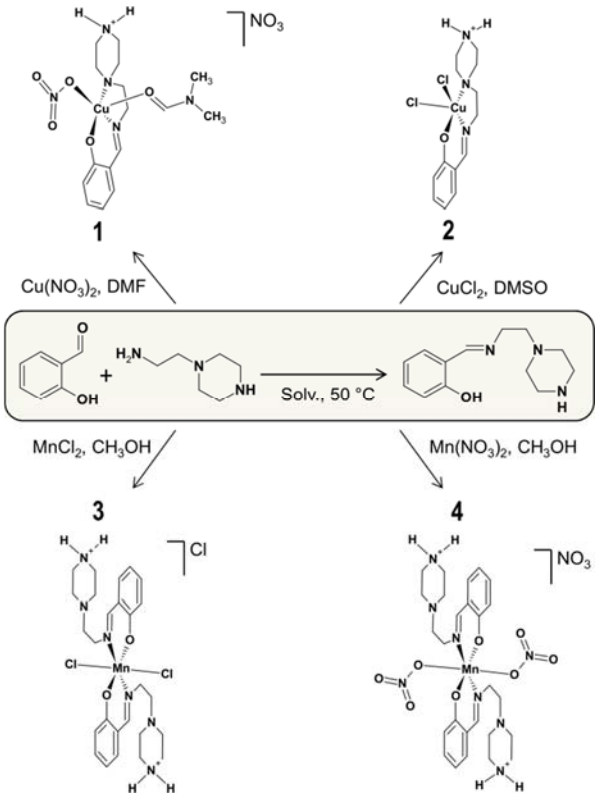


b

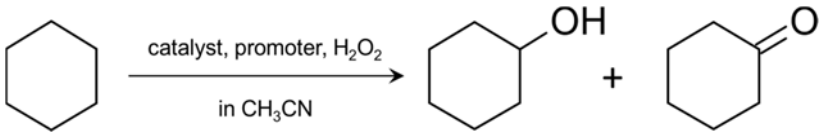


c

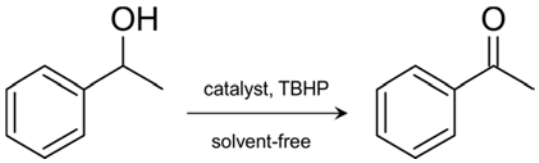
Figure 9. Influence of different additives (TEMPO, K_2CO_3, HNO_3, NHPI) (a), amount of catalyst (*b*) and temperature (*c*) on the yield of acetophenone in oxidation of 1-phenylethanol.



Scheme 1. Synthesis of the ligand HL and molecular structures of the coordination compounds obtained.



Scheme 2. Catalytic oxidation of cyclohexane with H_2O_2, catalysed by complexes **1**–**4**.



Scheme 3.Catalytic oxidation of 1-phenylethanol with TBPH (aqueous *tert*-butylhydroperoxide), catalysed by complexes **1**–**4**.

Table 1.Crystal data and structure refinement for **1**–**4**.

	1	**2**	**2a**	**3**	**4**
Chemical formula	$C_{16}H_{28}CuN_6O_9$	$C_{28}H_{44}Cl_4Cu_2N_6O_3S$	$C_{36}H_{68}Cl_4Cu_2N_6O_7S_5$	$C_{26}H_{38}Cl_3MnN_6O_2$	$C_{26}H_{40}MnN_9O_{12}$
Formula Mass	511.98	813.63	1126.14	627.91	725.61
Crystal system	Triclinic	Orthorhombic	Triclinic	Monoclinic	Triclinic
Space group	*P*–1	$P2_12_12_1$	*P*–1	*C*2/c	*P*–1
a (Å)	7.1594(3)	10.2134(15)	13.1833(10)	26.0272(11)	10.1352(12)
b (Å)	9.5551(4)	15.4327(17)	13.3291(9)	9.9491(4)	10.8985(12)
c (Å)	17.0683(7)	25.384(4)	14.7415(8)	14.2859(6)	15.8084(18)
α (°)	77.600(2)	90.00	86.717(2)	90.00	92.940(4)
β (°)	83.662(3)	90.00	88.068(3)	122.1670(10)	102.730(4)
γ (°)	72.835(3)	90.00	83.295(2)	90.00	96.087(3)
V (Å^3)	1088.21(8)	4001.0(9)	2567.5(3)	3131.5(2)	1688.6(3)
T (K)	150(2)	293(2)	150(2)	150(2)	150(2)
Z	2	4	2	4	2
Refl. total/ind./unique	11900/5313/4435	30026/8718/3434	26225/11291/5171	12063/3455/2685	9228/5905/2884
R_{int}	0.0282	0.2283	0.0870	0.0414	0.0535
Final R_1 ($I > 2\sigma(I)$)	0.0362	0.0860	0.0892	0.0379	0.0781
Final $wR(F^2)$ (all data)	0.0893	0.1941	0.2318	0.1032	0.1840
GOF	1.083	0.887	1.033	0.921	1.004

Table 2. Oxidation of cyclohexane with H_2O_2 catalysed by complexes **1**–**4** in the presence of various promoters.[a]

Promoter	Yields of products (%)[b]			
	1	**2**	**3**	**4**
HNO_3	4.6	14.8	0.1	0.1
HCl	12.4	11.2	< 0.1	< 0.1
H_2Ox[c]	< 0.1	< 0.1	< 0.1	< 0.1
Py[d]	21.6	15.3	0.3	0.2

[a] Conditions: $[catalyst]_0 = 1 \times 10^{-3}$ M, $[promoter]_0 = 0.01$ M, $[cyclohexane]_0 = 0.2$ M, $[H_2O_2]_0 = 1$ M, in acetonitrile at 50 °C, 3 h reaction time.[b] Sum of yields of cyclohexanol and cyclohexanone, based on the substrate, measured after addition of Ph_3P.[c] Oxalic acid.[d] Pyridine.

Table 3. Selected bond selectivity parameters in the oxidation of methylcyclohexane in acetonitrile.[a]

Catalytic system	1° : 2° : 3°	Proposed C–H attacking species	Ref
1 / Py / H_2O_2	1 : 2 : 16	HO•	–
2 / Py / H_2O_2	1 : 2 : 17	HO•	–
3 / Py / H_2O_2	1 : 4 : 30	HO•	–
4 / Py / H_2O_2	1 : 5 : 32	HO•	–
$[Co_4Fe_2O(L^1)_8]\cdot 4DMF\cdot H_2O$ / HNO_3 / H_2O_2	1 : 7 : 20	HO•	[20]
VO^{3-} / H_2SO_4/ H_2O_2	1 : 7 : 26	HO•	[53]
$[Os_3(CO)_{12}]$ / Py / H_2O_2	1 : 5 : 11	HO•	[40]
$[Mn_2L^2{}_2O_3]^{2+}$/ HOAc / H_2O_2	1 : 26 : 200	Mn^V=O	[42]
$[OCu_4(L^3)_4(BOH)_4][BF_4]_2$/ TBHP	1 : 16 : 128	*t*BuO•	[54]
$[(PhSiO_{1.5})_{10}(CuO)_2(NaO_{0.5})_2]$ / TBHP	1 : 12 : 93	*t*BuO•	[41]

[a] H_2L^1 = salicylidene-2-ethanolamine; L^2 = 1,4,7-trimethyl-1,4,7-triazacyclononane; H_3L^3 = triethanolamine.

Table 4. Solvent-free oxidation 1-phenylethanol using Cu(II) and Mn(III) catalysts.[a]

Entry	Catalyst	Catalyst amount [mol% *vs*. substrate]	Temperature [°C]	Additive[b]	Yield[c] [%]	TON[d]
1	**1**	0.05	80	–	12.3	246
2		0.05	80	TEMPO	14.4	288
3		0.05	80	K_2CO_3	26.1	522
4		0.05	80	HNO_3	trace	0
5		0.05	80	NHPI	17.4	348
6		0.1	80	K_2CO_3	46.0	460
7		0.1	50	K_2CO_3	18.2	182
8		0.1	100	K_2CO_3	62.0	620
9	**2**	0.05	80	–	23.4	468
10		0.05	80	TEMPO	22.0	440
11		0.05	80	K_2CO_3	30.0	600
12		0.05	80	HNO_3	12.2	244
13		0.05	80	NHPI	24.2	484
14		0.1	80	K_2CO_3	30.5	305
15		0.1	50	K_2CO_3	13.5	135
16		0.1	100	K_2CO_3	53.0	530
17	**3**	0.05	80	–	10.5	210
18		0.05	80	TEMPO[e]	17.9	358
19		0.05	80	K_2CO_3	18.0	360
20		0.05	80	HNO_3	trace	0
21		0.05	80	NHPI[f]	13.7	274
22		0.1	80	K_2CO_3	18.0	180
23		0.1	50	K_2CO_3	10.8	108
24		0.1	100	K_2CO_3	13.4	134
25	**4**	0.05	80	–	18.4	368
26		0.05	80	TEMPO	17.7	354
27		0.05	80	K_2CO_3	19.7	394
28		0.05	80	HNO_3	trace	0
29		0.05	80	NHPI	16.4	328
30		0.1	80	K_2CO_3	20.0	200
31		0.1	50	K_2CO_3	14.6	146
32		0.1	100	K_2CO_3	16.4	164
33	-	-	80	–	5.0	-
34	-	-	80	TEMPO	7.0	-
35	-	-	80	K_2CO_3	8.0	-

[a] Reaction conditions unless stated otherwise: 5 mmol of 1-phenylethanol, 2.5 or 5 μmol (0.05 or 0.1 mol% *vs*. substrate) of catalyst, 10 mmol of TBHP (2 eq. vs. substrate, 70% in H_2O). [b] 2.5 mol% vs. substrate. [c]Moles of ketone product per 100 mol of alcohol. [d] TON = Turnover number = number of moles of product per mol of catalyst. [e]TEMPO = 2,2,6,6-Tetramethyl-1-piperidinyloxy, free radical . [f]NHPI = N-hydroxyphthalimide.