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ARTICLE

Cobalt (III) sepulchrate complexes: application as sustainable oxidative catalysts

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The application of cobalt sepulchrate (sep) complexes as active and robust homogeneous catalysts is reported here for the first time, as well as the crystal structure of [Co(sep)]$_2$(SO$_4$)$_3$·5H$_2$O compound. The reaction chosen to investigate the catalytic performance of these catalysts was the oxidation of styrene because of the importance of its products in various industrial applications. Sustainable experimental conditions were selected, using H$_2$O$_2$ as oxidant and ionic liquids as solvents. Similar catalytic activity was found using complexes containing different anions: ([Co(sep)]Cl$_3$ and [Co(sep)]$_2$(SO$_4$)$_3$. Different kinetic profiles were found using different ionic liquids (1-butyl-3-methylimidazolium hexafluorophosphate or tetrafluoroborate) or acetonitrile as solvents. Complete conversions were achieved after 24 h of reaction. Benzaldehyde was the main product formed and in some cases the only one observed. The homogeneous cobalt catalysts using a ionic liquid as solvent could be recyclable for consecutive cycles without significant loss of activity. In addition, the stability of the cobalt sepulchrate complex was confirmed by ^{1}H NMR after catalytic use.

Introduction

The search of new efficient and selective catalytic systems capable to oxidise organic compounds under sustainable conditions is a research area of large interest. Catalytic oxidation of alkenes has attracted much attention for organic syntheses, since their products are among the most useful synthetic intermediates, as well as in industry processes. Oxidation is among the most important reactions in the chemical industry which is usually catalyzed by transition metal complexes. [1] In fact, it is well known the ability of the transition metal in activating oxidants.[2, 3] Cobalt(II) complexes have showed to be useful catalysts in oxidizing olefins since it

appears to be a good oxygen transfer agent.[4-10] Specifically, cobalt complexes have showed to catalyze alkylbenzenes with molecular oxygen, originating allylic oxidation products in the first step and consequently originating a high degree of cleaved products via autooxidation.[1] Reetz and Töllner demonstrated that Co(acac)$_3$ catalyzed the oxidation of styrene only to benzoic acid and benzaldehyde with O$_2$ in THF.[11] More recently, Wang et al. showed that different homogeneous Co(II) compounds are inactive for styrene oxidation using the same oxidant.[12] Environmentally friendly methods for oxidation of styrene with clean oxidant have been a subject of current research. [13-17] Besides the dioxygen, hydrogen peroxide is one of the most attractive oxidant because it is inexpensive, environmentally clean and easily handled. [18] However, the use of hydrogen peroxide for styrene oxidation catalyzed by homogeneous cobalt complexes is scarce and the most of these examples use polyoxometalates containing cobalt in their structures. [7, 8, 10] The nature of solvent is also a crucial aspect in the catalytic system to turn it more eco-sustainable. In recent years, replacing organic solvents with more environmentally benign solvents has attracted much attention. Many ionic liquids (ILs) have gained recognition as environmentally benign solvents due to their unique physical properties such as

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no-volatility, non-flammability and thermal stability.[19] The application of ionic liquids as solvents for catalytic styrene oxidation is scarce; however, few examples can be found showing the significant effect of these solvents in styrene conversion and selectivity.[13, 20-22]

In this work two Co(sep)[3+] complexes (sep = sepulchrate = 1,3,6,8,10,13,16,19 - octaazabicyclo[6.6.6]eicosane), [Co(sep)]$_2$(SO$_4$)$_3$ and [Co(sep)]Cl$_3$, were explored as catalysts for the oxidation of styrene with H$_2$O$_2$, using different solvents, acetonitrile (MeCN) and two 1-butyl-3-methylimidazolium (BMI) ionic liquids (ILs), BMIPF$_6$ and BMIBF$_4$. This type of complexes belong to the family of *cathrochelates*, where a metal ion (mainly transition metal ion) is encapsulated in a three-dimension polyazamacrocycle ligand cavity [23]. The presence of cage type ligands affects the nuclear motions which leads to peculiar electron transfer and spectroscopic properties [24, 25]. Co(sep)[3+] was firstly reported by Sargeson and co-workers [24, 26] and since then it has been studied as electron relay and photosensitizer for hydrogen generation from water [27-30], which is crucial for solar energy conversion, as redox mediators in photoelectrochemical cells [31], in graphene electrodes [32], in supramolecular arrays forming stable host-guest complexes with sulfonated calix[n]arenes (n=6 [31] and n=4 [32]), in nanotubes to make ionic devices [33] and in electro enzymatic processes [34-37]. However, to the best of our knowledge, their properties as catalysts for the oxidation of organic compounds have not yet been explored.

Experimental section

Materials and methods

Styrene (Aldrich), acetonitrile (MeCN, 99.5% Panreac), H$_2$O$_2$ (30%, Riedel de-Häen) and 1-butyl-3-methylimidazolium hexafluorophosphate (BMIPF$_6$, Aldrich) and tetrafluoroborate (BMIBF$_4$, Aldrich) were used without further purification

The GC-MS analyses were performed on Finnigan Trace GC-MS (Thermo Quest CE instruments) using helium as the carrier gas (35 cm/s); GC-FID was performed using a Varian Star 3400CX chromatograph to monitories catalytic reactions. The hydrogen was used as the carrier gas (55 cm/s) and fused silica Supelco capillary columns SPB-5 (30m x 0.25mm i.d.; 25 μm film thickness) were employed.

Synthesis of Cobalt (III) sepulchrate complexes

[Co(sep)][3+] complexes were prepared following a method described in literature [38] that allows first the precipitation of [Co(sep)][S$_2$CNEt$_2$]$_3$, ([S$_2$CNEt$_2$]$^-$ = diethyldithiocarbamate anion) and then [Co(sep)]Cl$_3$ and [Co(sep)]$_2$(SO$_4$)$_3$ were obtained by decomposition of diethyldithiocarbamate anion using hydrochloric acid and sulfuric acid, respectively. Crystals of [Co(sep)]$_2$(SO$_4$)$_3$ suitable for X-ray diffraction were obtained from slow evaporation of an concentrated aqueous solution (the complex was previously dissolved in hot water).

[Co(sep)]Cl$_3$: Anal. Calcd (%) for C$_{12}$H$_{30}$ Cl$_3$CoN$_8$.H$_2$O: C, 30.75; H, 6.67; N, 23.91. Found: C, 30.56; H, 6.70; N,

23.84. IR (KBr, cm^{-1}): 3040 (s) *(v*N-H and *v*C-H), 2851 (s) *(v*C-H capping groups), 412 (m) *(v*Co-N). ^{1}H NMR (D$_2$O, 400.13 MHz, 298 K): 3.9 (AB doublet pair, 12 H), 2.9 (AA'BB' pattern, 12H) ppm.

[Co(sep)]$_2$(SO$_4$)$_3$: Anal. Calcd (%) for C$_{24}$H$_{60}$Co$_2$N$_{16}$O$_{12}$S$_3$.5H$_2$O: C, 26.97; H, 6.60; N, 20.96. Found: C, 27.11; H, 6.19; N, 20.64. IR (KBr, cm^{-1}): 3044 (s) *(v*N-H and *v*C-H), 2844 (s) *(v*C-H capping groups), 1115 (s) *(v$_3$* SO$_4$$^{2-}$), 619 (s) *(v$_4$* SO$_4$$^{2-}$), 412 (m) *(v*Co-N). [1]H NMR (D$_2$O, 400.13 MHz, 298 K): 4.3 (AB doublet pair, 12 H), 3.4 (AA'BB' pattern, 12H) ppm.

Single crystal X-ray analysis

Crystalline material of the complex [Co(sep)]$_2$(SO$_4$)$_3$·10H$_2$O was manually harvested, and a suitable single crystal was mounted on a 0.2 mm cryo-loop using FOMBLIN Y perfluoropolyether vacuum oil (LVAC 25/6).[39] Diffraction data acquisition was performed on a Bruker X8 Kappa APEX II Charge-Coupled Device (CCD) area-detector diffractometer with the collection controlled by the APEX2 software package[40]: Mo K$_\alpha$ graphite-monochromated radiation, λ = 0.71073 Å; crystal was positioned at 35 mm from the detector and using 10 s of exposure time; temperature of acquisition (150 K) was set up with liquid nitrogen stream by the Oxford Cryosystems Series 700 monitored by the interface Cryopad[41]. Images were processed in the software SAINT+,[42] and absorption correction was carried out using the multi-scan semi-empirical method implemented in SADABS.[43] The structure was solved by the direct methods implemented in SHELXS-97,[44, 45] allowing the immediate identification of the Co- and S-atoms. The remaining C-, N- and O-atoms of the structure were further located from the difference Fourier maps calculated by successive full-matrix least-squares refinement cycles on F^2 using SHELXL-97,[45, 46] and were successfully refined with anisotropic displacement parameters.

H-atoms bonded to C-atoms of the sep ligand were positioned at their geometrical positions using appropriate *HFIX 23* instruction in SHELXL, and incorporated in subsequent refinement cycles in riding-motion approximation with isotropic thermal displacements parameters (U_{iso}) fixed at $1.2 \times U_{eq}$ of the respective C-atom. Furthermore, H-atoms attached to the N-atoms of the ligand and those of the crystallization water molecules were markedly visible in the difference Fourier maps, and included in subsequent refinement stages with the N–H distances restrained to 0.95(1) Å, the O–H and H···H distances restrained to 0.95(1) and 1.45(1) Å respectively (in order to ensure a chemically reasonable geometry for these molecules), and using a riding-motion approximation with an isotropic thermal displacement parameter fixed at $1.5 \times U_{eq}$ of the parent atom. Besides the identification and successful refinement of five crystallization water molecules the spaces originated by the close packing of complexes also contained some electron density, mainly due to disordered solvent molecules, which was not possible to modulate and refine properly. Searches for the total potential solvent area using the software package *PLATON* [47, 48] revealed

the existence of a cavity with a potential solvent accessible voids, and the original data set was then treated with the *SQUEEZE*[49] to remove the contribution of these highly disordered molecules in the solvent-accessible volume. The calculated solvent-free reflection list was then used for the final structure refinement.

Information of crystallographic data collection and structure refinement details is summarized in Table 1. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-981278. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 2EZ, U.K (FAX: +44 1223 336033), or online via *www.ccdc.cam.ac.uk/data_request/cif* or by emailing *data_request@ccdc.cam.ac.uk*.

Table 1. Crystal and structure refinement data for the complex $[Co(sep)]_2(SO_4)_3 \cdot 5H_2O$.

Formula	$C_{24}H_{80}Co_2N_{16}O_{22}S_3$
Mr	1159.08
Crystal morphology	Orange block
Crystal size /mm	$0.27 \times 0.16 \times 0.10$
Crystal system	Monoclinic
Space group	$C2/c$
a /Å	13.7348(10)
b /Å	11.2507(7)
c /Å	34.837(3)
α /°	90
β /°	91.443(4)
γ /°	90
Volume /Å^3	5381.5(7)
Z	18
$\rho_{calculated}$ /g cm^{-3}	1.431
$F(000)$	2456
μ /mm^{-1}	0.815
θ range /°	3.67 to 26.37
Index ranges	$-16 \leq h \leq 17$ $-14 \leq k \leq 13$ $-43 \leq l \leq 43$
Reflections collected	24177
Independent reflections	5462 ($R_{int} = 0.0489$)
Final R indices [I>2σ(I)]	$R_1 = 0.0492$; w$R_2 = 0.1116$
Final R indices (all data)	$R_1 = 0.0604$; w$R_2 = 0.1165$
Largest diff. peak and hole /e Å^3	0.692 and -0.471

Oxidation Reactions

The oxidation reactions of styrene were carried out under air (atmospheric pressure) in a closed borosilicate 5 mL reaction vessel equipped with a magnetic stirrer and immersed in a thermostated oil bath at 75 ºC. The catalytic reactions were performed using different solvents: MeCN and ionic liquids: 1-butyl-3-methylimidazolium hexafluorophosphate, BMIPF$_6$ and 1-butyl-3-methylimidazolium tetrafluoroborate, BMIBF$_4$. In a typical experiment, 3 µmol of cobalt catalyst (1.5 µmol of $[Co(sep)]_2(SO_4)_3$ or 3 µmol of $[Co(sep)]Cl_3$) were placed in the vessel, MeCN, BMIPF$_6$, BMIBF$_4$ (1,5 ml) was added and stirred. The substrate (1 mmol) was added and the reaction time was counted after the addition of H_2O_2 (4.5 mmol). The reactions were followed by GC analysis and stopped when a complete conversion of the substrate was observed or when the product yields remained constant after two successive GC analyses. At regular intervals, an aliquot was taken directly from the reaction mixture with a microsyringe, diluted in MeCN and injected into the GC or GC-MS equipment for analysis of starting materials and products.

Blank reactions were performed for both substrates, confirming that no oxidation products were obtained unless the catalyst and H_2O_2 are present.

The reactions carried out using the ionic liquid BMIPF$_6$ were regenerated and the homogeneous catalyst was recyclable. In view of that, the ionic liquid containing the catalyst was clean by adding a mixture of diethyl ether and ethyl acetate (1:1) and stirring for 10 min. The upper phase was removed and this procedure was repeated until the residual substrate and oxidative products present in the ionic liquid disappeared completely. Furthermore, the ionic liquid phase was left to dry in the oven at 40 ºC for several hours. After this procedure, the liquid phase containing the catalyst could be used in a new reaction cycle by adding the substrate and the oxidant.

Results and discussion

Co(sep) preparation and characterization

The complexes $[Co(sep)]Cl_3$ and $[Co(sep)]_2(SO_4)_3$ were obtained following a procedure described in literature [38] and characterized by elemental analysis, ^{1}H NMR and FTIR. Elemental analyses confirm the desired complexes formation. The ^{1}H NMR spectra of both compounds contains the typical shifts of Co(sep)$^{3+}$ [24], an AB doublet pair around 3.9 ppm for $[Co(sep)]Cl_3$ and around 4.3 ppm for $[Co(sep)]_2(SO_4)_3$ corresponding to the methylene protons in the cap and an AA'BB' pattern around 2.9 ppm for $[Co(sep)]Cl_3$ and around 3.4 ppm for $[Co(sep)]_2(SO_4)_3$ from the protons of ethylenediamine methylene groups. The infrared spectra exhibit the main vibrations of sepulchrate ligand as strong bands at 3040 cm^{-1} for $[Co(sep)]Cl_3$ and at 3044 cm^{-1} for $[Co(sep)]_2(SO_4)_3$ corresponding to the N-H and C-H stretching vibrations, and at 2851 cm^{-1} for $[Co(sep)]Cl_3$ and at 2844 cm^{-1} for $[Co(sep)]_2(SO_4)_3$ assigned to the capping methylene groups, and in both compounds the Co-N stretching vibrations appear at around 412 cm^{-1} as bands of medium intensity [50]. The presence of sulphate anions in $[Co(sep)]_2(SO4)_3$ is identified by strong bands at 1115 cm^{-1} and 619 cm^{-1} attributed to the stretching vibrations υ_3 and υ_4 of SO_4^{2-} anions, respectively.[51]

The synthesis of the Co(III) sep complex with the SO_4^- anion was unequivocally demonstrated by the crystal structure. Single-crystals with quality for X-ray diffraction (XRD) analysis were isolated by controlled recrystallization by cooling down a hot concentrated aqueous solution and the structure revealed a compound formulated as $[Co(sep)]_2(SO_4)_3 \cdot 10H_2O$. Unfortunately, several attempts and distinct procedures performed to obtain single-crystals appropriate for XRD analysis of the remaining compounds revealed to be unsuccessful. Interestingly, careful searches in the literature and in the Cambridge Structural Database (CSD, Version 5.33 2012, with two updates)[52, 53] reveal that despite the considerable number of studies involving metal complexes with sep ligands the number of crystal structures with this organic molecule is very (only twelve entries were found).[24, 26, 54-61]

The crystal structure of the compound $[Co(sep)]_2(SO_4)_3 \cdot 10H_2O$ was determined in the centrosymmetric monoclinic space group $C2/c$, with the asymmetric unit (asu) comprising one cationic complex $[Co(sep)]^{3+}$, one and a half sulphate anions and five crystallization water molecules (Figure 1). As characteristic of most of the transition metal complexes with the sep ligand, the Co(III) centre coordinates to the six N-atoms of the NH groups, ultimately originating a slightly distorted octahedral coordination geometry as demonstrated by the internal N−Co−N angles: while the *cis* angles range from 85.83(11) to 93.40(11)º, the three *trans* angles [174.82(11), 175.40(11) and 175.47(11)º] are very approximated of the linearity. Furthermore, all the distances Co−N are very close ranging from 1.978(3) to 1.993(3) Å, being comparable to that previous observed in identical $[Co(sep)]^{3+}$ complexes.[24, 56-61]

exclusively with the O-atoms of the sulfate anion, through various N−H⋯O hydrogen bounds, with the H⋯O distances found between 1.98(2) and 2.14(2) Å (green dashed lines in Figure 2a and 2b; geometric details about hydrogen bounds are summarized in Table 3). Additionally, the sulfate anions and the crystallization water molecules (O1W, O2W, O3W, O4W, O5W and O6W) establish numerous O−H⋯O hydrogen bounds, with H⋯O distances ranging from between 1.81(3) and 1.98(3) Å (yellow dashed lines in Figure 2a, 2b and 2c; see Table 3 for geometric details about these intermolecular interactions). The O−H⋯O interactions seems to have a strong character than the N−H⋯O hydrogen bonds. In this cooperative hydrogen bonding network, the $[Co(sep)]^{3+}$ complexes act exclusively as donor, through the NH groups and the sulfate anions behave solely as acceptor, while most of the crystallization water molecules present both donor and acceptor properties. Interestingly, the hydrogen bond interactions between the O1W, O2W, O3W, O4W and O5W waters [O2W–H4W⋯O1W^{iii}; O3W–H6W⋯O1W^{iii}; O4W–H7W⋯O3W^{iv} and O5W–H10W⋯O4W^{v}; symmetry operations: (iii) *x+1/2, y–1/2, z*; (iv) *x–1/2, y+1/2, z*, and (v) *x–1/2, y–1/2, z*] lead to the formation of a pentameric water cluster (Figure 2c). Ultimately, all the previous described intermolecular hydrogen bonding interactions lead to the formation of a 3D supramolecular network, with layers of the $[Co(sep)]^{3+}$ complexes extended in the [0 0 1] direction of the unit cell intercalated by the sulfate anions and water molecules (Figure 2b).

Table 2. Selected distances and angles of the Co(III) coordination centre of the complex $[Co(sep)]^{3+}$.

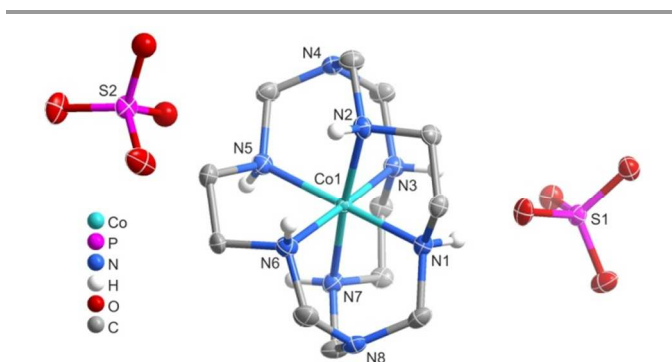| Distance /Å		Angles /°	
Co1−N1	1.987(3)	N1−Co1−N2	85.83(11)
Co1−N2	1.993(3)	N1−Co1−N3	93.40(11)
Co1−N3	1.975(3)	N1−Co1−N5	175.47(11)
Co1−N5	1.978(3)	N1−Co1−N6	90.52(11)
Co1−N6	1.989(3))	N1−Co1−N7	90.62(11)
Co1−N7	1.969(3)	N2−Co1−N3	90.83(11)
		N2−Co1−N5	91.16(11)
		N2−Co1−N6	92.82(11)
		N2−Co1−N7	175.40(11)
		N3−Co1−N5	90.03(11)
		N3−Co1−N6	174.82(11)
		N3−Co1−N7	86.45(11)
		N5−Co1−N6	86.24(11)
		N5−Co1−N7	92.56(11)
		N6−Co1−N7	90.13(11)

Figure 1. Crystal structure of the cationic complex $[Co(sep)]^{3+}$ and two sulphate anions (asu atoms represented as ellipsoids drawn at 50% probability level and the symmetry generated atoms shown in the ball-and-stick model), showing the labelling scheme for the metal coordination centre, all the N- and S-atoms. For simplicity motive only the H-atoms of the NH groups are drawn.

The $[Co(sep)]^{3+}$ complexes are surrounded by sulfate anions and numerous crystallization water molecules, being involved in an extensive inter-molecular hydrogen bonding network (Figure 2). In fact the NH groups of the Sep ligand interact
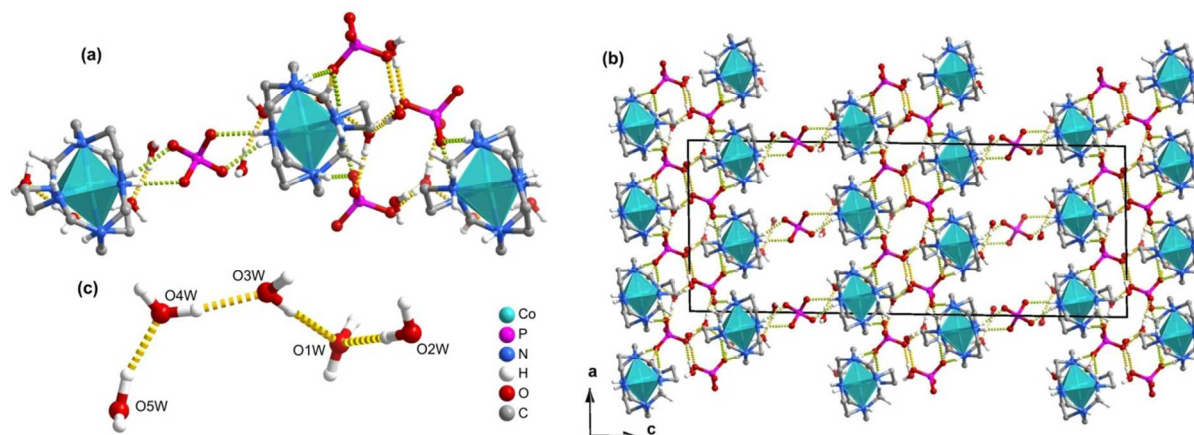
Figure 2. (a) N–H···O and O–H···O hydrogen bonding interactions involving three $[Co(sep)]^{3+}$ complexes with the adjacent sulphate anions and crystallization water molecules. **(b)** Crystal packing viewed in the [0 1 0] direction of the unit cell, revealing the 3D supramolecular network. **(c)** Pentameric $(H_2O)_5$ hydrogen bounded cluster. N–H···O and O–H···O are represented as green and yellow dashed lines, respectively, and for clarity reasons only the H-atoms involved directly in hydrogen bounds are drawn. Geometric details of the hydrogen bounds are listed in Table 3.

Table 3. Geometric information (distances in Å and angles in degrees) for the D–H···A hydrogen bond interactions of the $[Co(sep)]_2(SO_4)_3 \cdot 10H_2O$ crystal structure.[a]

C–H···O	d (H···A)	d (D···A)	∠(DHA)
O1W–H1W···O2[ii]	1.856(18)	2.744(3)	176(4)
O1W–H2W···O4	1.869(19)	2.754(4)	176(5)
O2W–H3W···O2	1.917(18)	2.794(3)	171(4)
O2W–H4W···O1W[iii]	1.968(19)	2.857(4)	172(4)
O3W–H5W···O1	1.89(2)	2.737(3)	153(4)
O3W–H6W···O1W[iii]	1.813(19)	2.717(4)	178(4)
O4W–H7W···O3W[iv]	1.82(3)	2.691(5)	166(7)
O5W–H10W···O4W[v]	1.81(3)	2.686(6)	163(7)
N1–H1···O2	1.98(2)	2.827(3)	168(4)
N2–H2···O1[v]	2.042(19)	2.912(3)	176(4)
N3–H3···O3	2.01(2)	2.834(3)	159(4)
N5–H5···O6[vi]	2.04(2)	2.836(4)	157(4)
N5–H5···O1[v]	2.14(2)	2.930(4)	151(3)
N7–H7···O5[vi]	2.01(2)	2.817(4)	157(4)

[a] Symmetry transformation used to generate equivalent atoms: (i) –x, y, –z+1/2; (ii) –x+1, –y+2, –z; (iii) x+1/2, y–1/2, z; (iv) x–1/2, y+1/2, z; (v) x–1/2, y–1/2, z; (vi) x+1/2, y+1/2, z.

Catalytic studies

The oxidation of styrene catalysed by $[Co(sep)]_2(SO_4)_3$ and $[Co(sep)]Cl_3$ was carried out in homogeneous phase using H_2O_2 as oxidant and different solvents: MeCN and two 1-butyl-3-methylimidazolium ionic liquids (ILs), $BMIPF_6$ and $BMIBF_4$.

In the absence of catalyst the conversion was negligible in the presence of different solvents; even after 24 h. Figure 3 compares the catalytic activity of $[Co(sep)]_2(SO_4)_3$ and $[Co(sep)]Cl_3$ for styrene oxidation using various solvent media. It is possible to conclude that $BMIBF_4$ is not a suitable solvent. However, using MeCN and $BMIPF_6$ almost complete conversion was achieved after 24 h of reaction. The significant difference of activity between the two ILs $BMIPF_6$ and $BMIBF_4$ was already observed before in the literature using Mn(II)-salen to catalyze styrene oxidation and the authors referred that this behaviour is associated to the polarity of the IL, because ILs with lower polarity have more affinity to styrene and facilitate the reaction.[21] Other examples in the literature also demonstrated that the anion of the ionic liquid presents an important effect on the activity of the catalyst.[62] The activity of both catalysts is comparable, what indicates that the different anion SO_4^{2-} and Cl^- seems do not have a strong influence in their catalytic performance for styrene oxidation. The kinetic profile of $[Co(sep)]Cl_3$ for styrene oxidation is exemplified in Figure 4 using the different solvents. In fact, a superior activity is observed since the first minutes of reaction when MeCN is used as solvent. This may be due to the solubility of the substrate and the oxidant in this solvent. Using MeCN medium, all the reactants are in the same phase what facilitates the catalytic oxidative reaction since the first minutes. In opposite, when $BMIPF_6$ is used as solvent, the oxidant H_2O_2 is not in the same liquid phase than the styrene and catalyst complex. The induction period observed for styrene oxidation catalyzed by cobalt sepulchrate complexes using $BMIPF_6$ as solvent may be caused by the immiscibility of the oxidant with this IL that contains the soluble cobalt catalyst and the substrate. One the other hand, the reason for the difference of activity in MeCN and $BMIPF_6$ media may be due to the presence of distinct active oxidant, since peroxyimidic acid can be formed by the reaction of MeCN with H_2O_2. These

active oxidant is well described in the literature for the catalyzed epoxidation reactions using MeCN and H_2O_2.[63]

The selectivity for the styrene oxidation showed to be less affected by the nature of the anion from the cobalt catalyst than the nature of the solvent. When MeCN was used as solvent the benzaldehyde (**1a**) was the only product formed in the presence of [Co(sep)]Cl$_3$ and when [Co(sep)]$_2$(SO$_4$)$_3$ was used as catalyst a small yield of acetophenone (**1c**) was also found from the first minutes of reaction (Table 4). Similar selectivity was achieved when MeCN was replaced by the ionic liquid BMIBF$_4$; however, in this case the conversion was not higher than 16% after 24 h of reaction. Higher conversions were found using BMIPF$_6$ but lower selectivity was achieved. In the presence of [Co(sep)]Cl$_3$ only benzaldehyde was formed until 6 h of reaction but after 24 h the benzoic acid (**1d**) was observed to be the main product formed and others such as benzaldehyde (**1a**), acetophenone (**1c**), phenylacetaldehyde (**1b**) and 2-hydroxy-1-phenylethanone (**1e**) were also formed.

When styrene oxidation was catalyzed by [Co(sep)]$_2$(SO$_4$)$_3$ the reaction was completed after 6 h and in this case only benzaldehyde (**1a**) and acetophenone (**1c**) were formed with practically equivalent yields. These results indicate that [Co(sep)]$_2$(SO$_4$)$_3$ is able to oxidize completely styrene in shorter time (6 h) than the [Co(sep)]Cl$_3$ (24 h) and also the [Co(sep)]$_2$(SO$_4$)$_3$ catalyst is more selective catalyst at the end of the reaction (52% of yield for benzaldehyde and 48% for acethophenone). However, if the reaction is left until 24 h, the yield of benzaldehyde (**1a**) and acetophenone (**1c**) decreases and benzoic acid and 2-hydroxy-1-phenylethanone (**1e**) are also formed (Table 4). Comparing the catalytic performance of the cobalt complexes in different solvents media it is possible to conclude that these are more selective catalysts in MeCN than in BMIPF$_6$. The presence of a different active oxidant such as peroxyimidic acid, formed by the interaction of H_2O_2 with MeCN solvent, may be the main reason for the difference of activity and also the selectivity of styrene oxidation in different media.
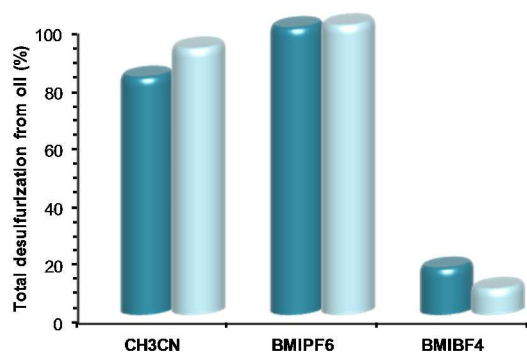

Figure 3. Conversion data for the oxidation of styrene obtained after 24 h when catalyzed by [Co(sep)]Cl$_3$ (dark blue) and [Co(sep)]$_2$(SO$_4$)$_3$ (light blue) using different solvents (CH$_3$CN, BMIPF$_6$ and BMIBF$_4$) and H_2O_2 as oxidant.
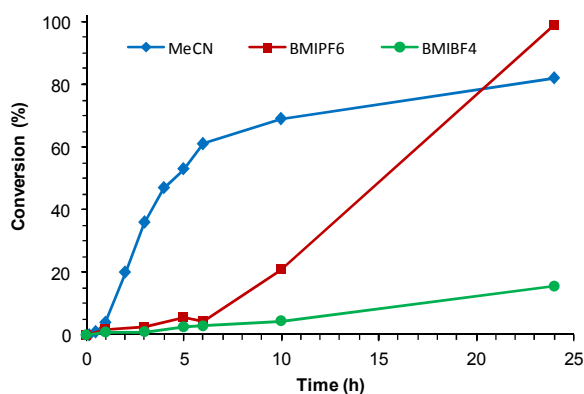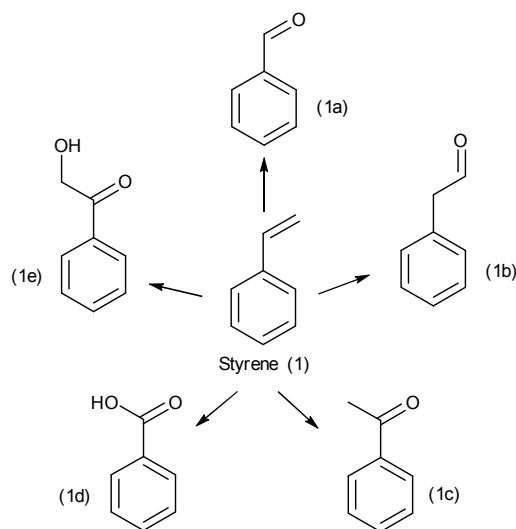

Figure 4. Kinetic profile for the oxidation of styrene catalyzed by [Co(sep)]Cl$_3$ using different solvents and H_2O_2 as oxidant at 75 ºC.

Scheme 1

When cobalt-polyoxometalates were used as homogeneous catalysts for styrene oxidation using H_2O_2 as oxidant and MeCN as solvent the main product obtained was also benzaldehyde. [7, 8, 10] The oxidation of styrene to benzaldehyde with H_2O_2 catalyzed by these type of inorganic complexes is well documented in the literature. The mechanism proceeds initially by the interaction of H_2O_2 with the metal center, generating active peroxo species. A mechanistic suggestion was also presented recently for Co(II) complexes in the presence of O_2 and also in this case a superoxo complex was formed.[64] Afterwards, styrene is bonded to produce a peroxometallocycle and in the next step styrene oxide is formed. A further nucleophilic attack of H_2O_2 on the styrene oxide originates benzaldehyde.[65, 66] The phenylacetaldehyde is possible formed through isomerisation of styrene oxide, while the formation of

benzoic acid from benzaldehyde is a simple oxidation.[67] In the literature is proposed that the formation of acetophenone could also be facilitated by direct oxidative cleavage of the vinyl double bond of styrene, via a radical mechanism.[68] The formation of 2-hydroxy-1-phenylethanone from styrene oxidation was investigated recently using similar experimental conditions as used in the present work.[69] From this research it was found that 2-hydroxy-1-phenylethanone and acetophenone are formed from the oxidation of styrene oxide and this is probably the main reason why this last was not observed as by product in our work.

Table 4. The yield of the various products obtained after 24 h of styrene oxidation using $[Co(sep)]Cl_3$ and $[Co(sep)]_2(SO_4)_3$ as catalysts and different solvent media.

	$[Co(sep)]Cl_3$					$[Co(sep)]_2(SO_4)_3$				
	1a	1b	1c	1d	1e	1a	1b	1c	1d	1e
MeCN	82	-	-	-	-	80	-	12	-	-
BMIBF$_4$	16	-	-	-	-	9	-	-	-	-
1st -BMIPF$_6$ [a]	11	12	25	32	19	25	19	18	29	9
2nd -BMIPF$_6$ [b]	6	8	1	63	22	23	13	29	26	-
3rd -BMIPF$_6$ [c]	4	8	1	31	21	16	22	7	33	17

[a] First reaction cycle.   [b] Second reaction cycle.   [c] Third reaction cycle.

Catalyst recyclability and stability

The reusability of the homogeneous catalysts is normally difficult because of the trouble of its isolation from reaction medium. In the present work, the reusability of the homogeneous $[Co(sep)]Cl_3$ and $[Co(sep)]_2(SO_4)_3$ was investigated for the catalytic systems using BMIPF$_6$. After the complete oxidation of styrene from the first reaction cycle, the organic products were removed from reaction medium by adding a mixture of 1:1 diethyl ether and ethyl acetate that was left to stir for 10 min at room temperature. This extraction process was repeated until no organic products were detected in the BMIPF$_6$ medium. After this process, the IL phase containing the cobalt catalyst was dried for several hours at 40 ºC to remove residual water originating from the oxidant solution. After this, another reaction cycle was performed by adding the substrate and the oxidant to the clean BMIPF$_6$ solution already containing the cobalt complex.
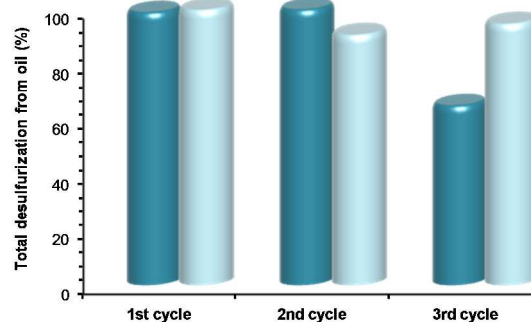

Figure 5. Conversion data obtained after 24 h for three consecutive cycles for the oxidation of styrene catalyzed by cobalt complexes $[Co(sep)]Cl_3$ (dark blue) and $[Co(sep)]_2(SO_4)_3$ (light blue)] using the ionic liquid BMIPF$_6$ as solvent and H$_2$O$_2$ as oxidant at 75 ºC.

Figure 5 display the conversion data obtained after 24 h of styrene oxidation catalyzed by $[Co(sep)]Cl_3$ and $[Co(sep)]_2(SO_4)_3$. It can be observed that a small decrease of activity is only noticed in the presence of $[Co(sep)]Cl_3$ after the third reaction cycle. However, in the presence of $[Co(sep)]_2(SO_4)_3$ almost no deactivation was detected between reaction cycles. Table 4 presents the yields for the different products obtained for the different cycles after 24 h of reaction. It is important to mention that the near completion of styrene oxidation catalyzed by $[Co(sep)]_2(SO_4)_3$/BMIPF$_6$ system was observed only after 24 h of reaction for the second and the third reaction cycle. This is probably due to a small loss of catalyst during the product extraction process performed after each reaction cycle.
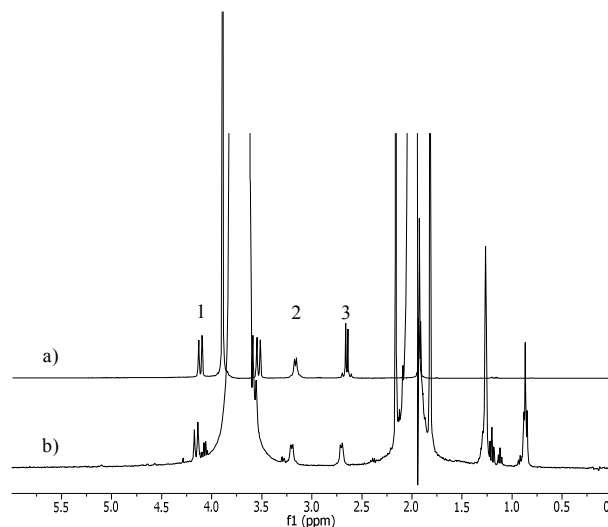

Figure 6. a) ^{1}H NMR spectrum of $[Co(sep)]_2(SO_4)_3$ in CD$_3$CN and D$_2$O in the same ratio used in catalytic experiments. **b)** ^{1}H NMR spectrum of $[Co(sep)]_2(SO_4)_3$ after catalytic use for styrene oxidation. **1)** one doublet from protons of capping methylene groups **2)** and **3)** two multiplets from protons of methylene of ethylenediamine groups.

The stability of the complex $[Co(sep)]_2(SO_4)_3$ after catalysis was verified by ^{1}H NMR spectroscopy under the same conditions used in the catalytic experiments. The ^{1}H spectrum shows undoubtedly one doublet corresponding to the methylene groups in the cap (the other is not seen with clarity due to the overlapping of the solvent signal) and the AA'BB' pattern of the protons of ethylenediamine methylene groups of sepulchrate ligand (Figure 6) In addition to the high catalytic performance of the $[Co(sep)]_2(SO_4)_3$ catalyst, the results of ^{1}H NMR performed after catalytic use indicate that these are stable cobalt complexes in the presence of an excess of H_2O_2 oxidant.

Conclusions

Cobalt (III) sepulchrate complexes containing two different anions ($[Co(sep)]Cl_3$ and $[Co(sep)]_2(SO_4)_3$ were successfully prepared and characterized by elemental analysis, FT-IR and ^{1}H NMR. Furthermore, during the synthesis of $[Co(sep)]_2(SO_4)_3$ single-crystals with high quality were obtained and a detailed structural characterization could be performed for this complex. Both cobalt complexes showed to be able to catalyze the oxidation of styrene using H_2O_2 as oxidant and acetonitrile or 1-butyl-3-methylimidazolium hexafluorophosphate (BMIPF$_6$) as solvent. A superior catalytic activity for the first hours of reaction was observed using acetonitrile as solvent, which must be related to the solubility of catalyst, oxidant and substrate in this solvent. In opposite, an induction period was observed when BMIPF$_6$ was used, probably caused by the immiscibility of the H_2O_2 with this ionic liquid containing the catalyst and the substrate. However, after 24 h of reaction a complete conversion of styrene was observed in the presence of both cobalt complexes in BMIPF$_6$. Near complete conversion was also achieved using acetonitrile (92 and 82% in the presence of $[Co(sep)]_2(SO_4)_3$ and $[Co(sep)]Cl_3$, respectively). The selectivity obtained in the presence of acetonitrile was higher than when BMIPF$_6$ was used, since in the first case only benzaldehyde (yield of 80%) and a small amount of acetophenone (yield of 12%) was formed when catalyzed by $[Co(sep)]_2(SO_4)_3$. The system using BMIPF$_6$ was less selective but able to be recyclable for consecutive cycles without significant loss of activity. Furthermore, the stability of cobalt sepulchrate catalysts was confirmed after catalytic use by ^{1}H NMR, demonstrating the viability and efficiency of these unexplored catalysts for the oxidation of styrene. Further work will be developed using these complexes as promising active and robust catalysts to oxidize other valuable substrates.

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