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Introduction

The search for new efficient and selective catalytic systems capable of oxidising 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, the ability of the transition metals to activate oxidants is well known.^{2,3} Cobalt(π) complexes have been shown to be useful catalysts for oxidizing olefins since they appear to be good oxygen transfer agents.⁴⁻¹⁰ Specifically, cobalt complexes have been shown to catalyze the oxidation of alkylbenzenes with molecular oxygen, giving rise to allylic oxidation products in the first step and consequently a high degree of cleaved products via autooxidation.¹ Reetz and Töllner demonstrated that Co(acac)₃ catalyzed the oxidation of styrene resulting in the formation of only benzoic acid and benzaldehyde with O2 in THF.11 More recently, Wang et al. showed that different homogeneous Co(II)

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 the $[Co(sep)]_2(SO_4)_3\cdot 10H_2O$ compound. The reaction chosen to investigate the catalytic performance of these catalysts was the oxidation of styrene due to the importance of its products in various industrial applications. Sustainable experimental conditions were selected, using H_2O_2 as the oxidant and ionic liquids as solvents. A 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 an ionic liquid as solvent could be recycled for consecutive cycles without significant loss of activity. In addition, the stability of the cobalt sepulchrate complex was confirmed by ¹H NMR after catalytic use.

compounds are inactive for styrene oxidation using the same oxidant.12 Environmentally friendly methods for oxidation of styrene with a clean oxidant have been a subject of current research.13-17 Besides dioxygen, hydrogen peroxide is one of the most attractive oxidants 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 most of these examples use polyoxometalates containing cobalt in their structures.^{7,8,10} The nature of solvent is also a crucial aspect of 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 non-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 on 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 H₂O₂, using different solvents, acetonitrile (MeCN) and two 1-butyl-3-methylimidazolium (BMI) ionic liquids (ILs), BMIPF₆ and BMIBF₄. These types of complexes belong to the family of *cathrochelates*, where a metal ion (mainly a transition metal ion) is encapsulated in a three-dimensional polyaza-macrocycle ligand cavity.²³ The presence of cage type ligands affects the nuclear motions which leads to peculiar electron

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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 an electron relay and photosensitizer for hydrogen generation from water,^{27–30} which is crucial for solar energy conversion, as a redox mediator 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 devices³³ and in electroenzymatic processes.^{34–37} However, to the best of our knowledge, its properties as a catalyst for the oxidation of organic compounds have not yet been explored.

Experimental section

Materials and methods

Styrene (Aldrich), acetonitrile (MeCN, 99.5% Panreac), H_2O_2 (30%, Riedel de-Häen) and 1-butyl-3-methylimidazolium hexafluorophosphate (BMIPF₆, Aldrich) and tetrafluoroborate (BMIBF₄, Aldrich) were used without further purification The GC-MS analyses were performed on a Finnigan Trace GC-MS (Thermo Quest CE instruments) using helium as the carrier gas (35 cm s⁻¹); GC-FID was performed using a Varian Star 3400CX chromatograph to monitor catalytic reactions. Hydrogen was used as the carrier gas (55 cm s⁻¹) and fused silica Supelco capillary columns SPB-5 (30 m × 0.25 mm 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 the literature³⁸ that allows first the precipitation of [Co(sep)]- $[S_2CNEt_2]_3$, $([S_2CNEt_2]^- =$ diethyldithiocarbamate anion) and then $[Co(sep)]Cl_3$ and $[Co(sep)]_2(SO_4)_3$ were obtained by decomposition of the diethyldithiocarbamate anion using hydrochloric acid and sulfuric acid, respectively. Crystals of $[Co(sep)]_2(SO_4)_3$ suitable for X-ray diffraction were obtained by slow evaporation of a concentrated aqueous solution (the complex was previously dissolved in hot water).

[Co(sep)]Cl₃. Anal. calcd (%) for $C_{12}H_{30}Cl_3CoN_8 H_2O$: 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) (ν N–H and ν C–H), 2851 (s) (ν C–H capping groups), 412 (m) (ν Co–N). ¹H NMR (D₂O, 400.13 MHz, 298 K): 3.9 (AB doublet pair, 12H), 2.9 (AA'BB' pattern, 12H) ppm.

 $[Co(sep)]_2(SO_4)_3$. Anal. calcd (%) for $C_{24}H_{60}Co_2N_{16}O_{12}S_3$ ·5H₂O: 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) (ν N–H and ν C–H), 2844 (s) (ν C–H capping groups), 1115 (s) (ν_3 SO₄^{2–}), 619 (s) (ν_4 SO₄^{2–}), 412 (m) (ν Co–N). ¹H NMR (D₂O, 400.13 MHz, 298 K): 4.3 (AB doublet pair, 12H), 3.4 (AA'BB' pattern, 12H) ppm.

Single crystal X-ray diffraction

Crystalline material of the complex $[Co(sep)]_2(SO_4)_3$.10H₂O 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 using the APEX2 software package:⁴⁰ Mo K_a graphitemonochromated radiation, $\lambda = 0.71073$ Å; the crystal was positioned at 35 mm from the detector with 10 s of exposure time; temperature of acquisition (150 K) was set up with liquid nitrogen stream using the Oxford Cryosystems Series 700 monitored using 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 successfully refined using 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 displacement parameters ($U_{\rm iso}$) fixed at 1.2 \times $U_{\rm eq}$ 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 $H \cdots H$ 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 SQUEEZE⁴⁹ 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 are summarized in Table 1.

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 °C. The catalytic reactions were performed using different solvents: MeCN and ionic liquids: 1-butyl-3-methylimidazolium hexafluorophosphate, BMIPF₆ and 1-butyl-3-methylimidazolium tetrafluoroborate, BMIBF₄. In a typical experiment, 3 µmol of a 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, and MeCN, BMIPF₆, and BMIBF₄ (1.5 mL) were added

Table 1 Crystal and structure refinement data for the complex $[Co(sep)]_2(SO_4)_3$ 10H₂O

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Formula	$C_{24}H_{80}Co_2N_{16}O_{22}S_3$
$M_{ m r}$	1159.08
Crystal morphology	Orange block
Crystal size/mm	0.27 imes 0.16 imes 0.10
Crystal system	Monoclinic
Space group	C2/c
$a/ m \AA$	13.7348(10)
b/Å	11.2507(7)
c/Å	34.837(3)
$\alpha/^{\circ}$	90
$\beta/^{\circ}$	91.443(4)
γ/°	90
Volume/Å ³	5381.5(7)
Ζ	18
$\rho_{\rm calculated}/{\rm g \ cm^{-3}}$	1.431
F(000)	2456
μ/mm^{-1}	0.815
θ range/°	3.67 to 26.37
Index ranges	$-16 \leq h \leq 17$
U	$-14 \leq k \leq 13$
	$-43 \leq l \leq 43$
Reflections collected	24 177
Independent reflections	5462 ($R_{\rm int} = 0.0489$)
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0492; wR_2 = 0.1116$
Final <i>R</i> 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
0 r	

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 using a microsyringe, diluted with 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 BMIPF₆ were regenerated and the homogeneous catalyst was recyclable. In view of that, the ionic liquid containing the catalyst was cleaned 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 °C 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 the literature³⁸ and characterized by elemental analysis, ¹H NMR and FTIR spectroscopy. Elemental analyses confirm the desired complex formation. The ¹H NMR spectra of both compounds contain the typical

shifts of $Co(sep)^{3+}$,²⁴ an AB doublet pair at around 3.9 ppm for [Co(sep)]Cl₃ and at around 4.3 ppm for [Co(sep)]₂(SO₄)₃ corresponding to the methylene protons in the cap and an AA'BB' pattern around 2.9 ppm for [Co(sep)]Cl₃ 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 $[Co(sep)]_2(SO_4)_3$ is identified by strong bands at 1115 cm⁻¹ and 619 cm⁻¹ attributed to the stretching vibrations ν_3 and ν_4 of SO₄²⁻ anions, respectively.⁵¹

The synthesis of the Co(III) sep complex with the SO₄⁻ anion was unequivocally demonstrated by the crystal structure. Singlecrystals 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 complexes revealed to be unsuccessful. Interestingly, careful searches in the literature and in the Cambridge Structural Database (CSD, Version 5.34 2013)^{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 low (only twelve entries were found).^{24,26,54-61}

The crystal structure of the compound $[Co(sep)]_2(SO_4)_310H_2O$ was determined to belong to 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 (Fig. 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 giving rise to a slightly distorted octahedral

Fig. 1 Crystal structure of the cationic complex $[Co(sep)]^{3+}$ and two sulphate anions (asu atoms represented as ellipsoids drawn at the 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 purposes, only the H-atoms of the NH groups are drawn.

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

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)

coordination geometry as demonstrated by the internal N–Co–N angles: while the *cis* angles range from 85.83(11) to 93.40(11)°, the three *trans* angles [174.82(11), 175.40(11) and 175.47(11)°] are very approximated to linearity. Furthermore, all the distances Co–N are very close ranging from 1.978(3) to 1.993(3) Å, being comparable to that previously observed in identical $[Co(sep)]^{3+}$ complexes (Table 2).^{24,56–61}

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 (Fig. 2). In fact the NH groups of the sep ligand interact exclusively with the O-atoms of the sulfate anion, through various N–H···O hydrogen bonds, with the H···O distances found between 1.98(2) and 2.14(2) Å (green dashed lines in Fig. 2a and b; geometric details about hydrogen bonds are summarized in Table 3). Additionally, the sulfate anions and the crystallization water molecules (O1W, O2W, O3W, O4W and 5W) establish numerous O–H···O hydrogen bonds, with H···O distances ranging from 1.81(3) to 1.98(3) Å (yellow dashed lines in Fig. 2a–c; see Table 3 for geometric details

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

С–Н…О	$d(\mathbf{H} \cdot \cdot \cdot \mathbf{A})$	$d(\mathbf{D}\cdot\cdot\cdot\mathbf{A})$	∠(DHA)
O1W−H1W···O2 ⁱ	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 ⁱⁱ	1.968(19)	2.857(4)	172(4)
O3W−H5W···O1	1.89(2)	2.737(3)	153(4)
O3W−H6W· · · O1W ⁱⁱ	1.813(19)	2.717(4)	178(4)
O4W−H7W· · · O3W ⁱⁱⁱ	1.82(3)	2.691(5)	166(7)
$O5W-H10W \cdot \cdot \cdot O4W^{iv}$	1.81(3)	2.686(6)	163(7)
N1-H1···O2	1.98(2)	2.827(3)	168(4)
$N2-H2 \cdot \cdot \cdot O1^{iv}$	2.042(19)	2.912(3)	176(4)
N3-H3···O3	2.01(2)	2.834(3)	159(4)
$N5-H5\cdots O6^{v}$	2.04(2)	2.836(4)	157(4)
N5−H5···O1 ^{iv}	2.14(2)	2.930(4)	151(3)
$N7-H7\cdots O5^{v}$	2.01(2)	2.817(4)	157(4)

^{*a*} Symmetry transformation used to generate equivalent atoms: (i) -x + 1, -y + 2, -z; (ii) x + 1/2, y - 1/2, 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.

about these intermolecular interactions). The O-H···O interactions seem to be stronger than the N-H-··O hydrogen bonds. In this cooperative hydrogen bonding network, the $[Co(sep)]^{3+}$ complexes act exclusively as donors, though the NH groups and the sulfate anions behave solely as acceptors, 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 water molecules [O2W-H4W···O1Wⁱⁱ; O3W-H6W···O1Wⁱⁱ; O4W-H7W···O3Wⁱⁱⁱ and O5W-H10W···O4W^{iv}; symmetry operations: (ii) x + 1/2, $y - \frac{1}{2}$, z; (iii) $x - \frac{1}{2}$, $y + \frac{1}{2}$, z, and (iv) $x - \frac{1}{2}$, $y - \frac{1}{2}$, z] lead to the formation of a pentameric water cluster (Fig. 2c). Ultimately, all the previously 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 (Fig. 2b).



Fig. 2 (a) $N-H\cdotsO$ and $O-H\cdotsO$ hydrogen bonding interactions involving three $[Co(sep)]^{3+}$ complexes with the adjacent sulphate anions and crystallization water molecules. (b) Crystal packing viewed in the [010] direction of the unit cell, revealing the 3D supramolecular network. (c) Pentameric $(H_2O)_5$ hydrogen bonded cluster. $N-H\cdotsO$ and $O-H\cdotsO$ are represented as green and yellow dashed lines, respectively, and for clarity reasons only the H-atoms involved directly in hydrogen bonding are drawn. Geometric details of the hydrogen bonds are listed in Table 3.

Catalytic studies

The oxidation of styrene catalysed by $[Co(sep)]_2(SO_4)_3$ and [Co(sep)]Cl₃ was carried out in the homogeneous phase using H₂O₂ as the oxidant and different solvents: MeCN and two 1-butyl-3-methylimidazolium ILs, BMIPF₆ and BMIBF₄. In the absence of a catalyst the conversion was negligible in the presence of different solvents, even after 24 h. Fig. 3 compares the catalytic activity of [Co(sep)]₂(SO₄)₃ and [Co(sep)]Cl₃ for styrene oxidation using various solvent media. It is possible to conclude that BMIBF₄ is not a suitable solvent. However, using MeCN and BMIPF₆ almost complete conversion was achieved after 24 h of reaction. The significant difference in activity between the two ILs BMIPF₆ and BMIBF₄ was already observed before in the literature using Mn(II)-salen to catalyze styrene oxidation and the authors showed that this behaviour is associated with the polarity of the ILs, because ILs with lower polarity have more affinity to styrene and facilitate the reaction.²¹ Other examples also demonstrated that the anion of the IL presents an important effect on the activity of the catalyst.⁶² The activity of both catalysts is comparable, which indicates that the different anions SO_4^{2-} and Cl^- do not have a strong influence on their catalytic performance for styrene oxidation. The kinetic profile of [Co(sep)]Cl₃ for styrene oxidation is exemplified in Fig. 4 using the different solvents. In fact, a superior activity is



Fig. 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 (CH₃CN, BMIPF₆ and BMIBF₄) and H₂O₂ as the oxidant.



Fig. 4 Kinetic profile for the oxidation of styrene catalyzed by $[Co(sep)]Cl_3$ using different solvents and H_2O_2 as the oxidant at 75 °C.

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. In this case, all the reactants are in the same phase, which facilitates the catalytic oxidative reaction in minutes. In contrast, when BMIPF₆ is used as solvent, the oxidant H_2O_2 is not in the same liquid phase as the styrene and catalyst complex. The induction period observed for styrene oxidation catalyzed by cobalt sepulchrate complexes using BMIPF₆ as solvent may be caused by the immiscibility of the oxidant with this IL that contains the soluble cobalt catalyst and the substrate. On the other hand, the reason for the difference in activity in MeCN and BMIPF₆ media may be due to the presence of a distinct active oxidant, since peroxyimidic acid can be formed by the reaction of MeCN with H₂O₂. This active oxidant is well described in the literature for the catalyzed epoxidation reactions using MeCN and H₂O₂.⁶³

The selectivity for the styrene oxidation was shown 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 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 low yield of acetophenone (1c) was also found from the first minutes of reaction (Table 4). A similar selectivity was attained when MeCN was replaced by the ionic liquid BMIBF₄; however, in this case the conversion was not higher than 16% after 24 h of reaction. Higher conversions were found using BMIPF₆ but lower selectivity was achieved. In the presence of [Co(sep)]Cl₃ 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 (Scheme 1).

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 $[Co(sep)]Cl_3 (24 h)$ and also the $[Co(sep)]_2(SO_4)_3$ catalyst is more selective at the end of the reaction (52% of yield for benzaldehyde (**1a**) and 48% for acetophenone (**1c**)). 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).

Table 4The yield of the various products obtained after 24 h of styreneoxidation using $[Co(sep)]Cl_3$ and $[Co(sep)]_2(SO_4)_3$ as catalysts and differentsolvent 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		_	_	_
1^{st} -BMIPF ₆ ^a	11	12	25	32	19	25	19	18	29	9
2^{nd} -BMIPF ₆ ^b	6	8	1	63	22	23	13	29	26	_
3^{rd} -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.



Comparing the catalytic performance of the cobalt complexes in different solvent media it is possible to conclude that these are more selective catalysts in MeCN than in BMIPF₆. 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 in activity and also the selectivity of styrene oxidation in different media.

When cobalt-polyoxometalates were used as homogeneous catalysts for styrene oxidation using H2O2 as oxidant and MeCN as solvent the main product obtained was also benzaldehyde.^{7,8,10} The oxidation of styrene to benzaldehyde with H₂O₂ catalyzed by these types 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 H₂O₂ on the styrene oxide gives rise to benzaldehyde.^{65,66} Phenylacetaldehyde is possibly formed through isomerisation of styrene oxide, while the formation of benzoic acid from benzaldehyde occurs via a simple oxidation reaction.⁶⁷ In the literature it 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 under similar experimental conditions to those used in the present work.⁶⁹ From this research it was found that 2-hydroxy-1-phenylethanone and acetophenone are formed by the oxidation of styrene oxide and this is probably the main reason why the latter was not observed as a by product in our work.

Catalyst recyclability and stability

The reusability of the homogeneous catalysts is normally arduous because of the difficulty in isolating them 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 BMIPF₆. 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 BMIPF₆ medium. After this process, the IL phase containing the cobalt catalyst was dried for several hours at 40 °C to remove residual water originated from the oxidant solution. After this, another reaction cycle was performed adding the substrate and the oxidant to the clean BMIPF₆ solution already containing the cobalt complex.

Fig. 5 shows 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 the $[Co(sep)]_2(SO_4)_3/BMIPF_6$ system was observed only after 24 h of reaction for the second and the third reaction cycles. This is probably due to a small loss of the catalyst during the product extraction process performed after each reaction cycle.

The stability of the complex $[Co(sep)]_2(SO_4)_3$ after catalysis was verified by ¹H NMR spectroscopy under the same conditions used in the catalytic experiments. The ¹H 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 (Fig. 6) In addition to the high catalytic performance of the $[Co(sep)]_2(SO_4)_3$ catalyst, the results of ¹H NMR performed after catalytic use indicates that this is a stable cobalt complex in the presence of an excess of the H₂O₂ oxidant.



Fig. 5 Conversion data obtained after 24 h for three consecutive cycles for the oxidation of styrene catalyzed by cobalt complexes [Co(sep)]Cl₃ (dark blue) and [Co(sep)]₂(SO₄)₃ (light blue) using the IL BMIPF₆ as solvent and H₂O₂ as the oxidant at 75 °C.



Fig. 6 (a) ¹H NMR spectrum of $[Co(sep)]_2(SO_4)_3$ in CD₃CN and D₂O in the same ratio used in catalytic experiments. (b) ¹H 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.

Conclusions

Cobalt(m) sepulchrate complexes containing two different anions [Co(sep)]Cl₃ and [Co(sep)]₂(SO₄)₃ were successfully prepared and characterized by elemental analysis, FT-IR and ¹H NMR. Furthermore, during the synthesis of [Co(sep)]₂(SO₄)₃ singlecrystals with high quality were isolated and a detailed structural characterization could be performed for this complex. The two cobalt complexes were able to catalyze the oxidation of styrene using H₂O₂ as the oxidant and acetonitrile or 1-butyl-3-methylimidazolium hexafluorophosphate (BMIPF₆) as solvent. A superior catalytic activity in the first hours of reaction was observed using acetonitrile as solvent, which must be related to the solubility of the catalyst, the oxidant and the substrate in this solvent. In contrast, an induction period was observed when BMIPF₆ was used, probably caused by the immiscibility of H₂O₂ with this IL containing the catalyst and the substrate. However, after 24 h of reaction a complete conversion of styrene was attained in the presence of both cobalt complexes in BMIPF₆. 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 BMIPF₆ was used, since in the first case only benzaldehyde (yield of 80%) and a small amount of acetophenone (yield of 12%) were formed when catalyzed by $[Co(sep)]_2(SO_4)_3$. The system using BMIPF₆ was less selective but was able to be recycled for consecutive cycles without significant loss of activity. Furthermore, the stability of cobalt sepulchrate catalysts was confirmed after catalytic use by ¹H 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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References

- 1 R. A. Sheldon and J. K. Kochi, *Metal-catalyzed oxidations of organic compounds*, Academic Press, New York, 1981.
- 2 R. H. Crabtree, *Encyclopedia of Inorganic Chemistry*, John Wiley & Sons, Ltd, 2006.
- 3 K. C. Gupta and A. K. Sutar, *Coord. Chem. Rev.*, 2008, 252, 1420–1450.
- 4 B. Tamami and S. Ghasemi, Appl. Catal., A, 2011, 393, 242–250.
- 5 E. Angelescu, R. Ionescu, O. D. Pavel, R. Zavoianu, R. Birjega, C. R. Luculescu, M. Florea and R. Olar, *J. Mol. Catal. A: Chem.*, 2010, **315**, 178–186.
- 6 T. Qiu, X. Y. Xu and X. H. Qian, J. Chem. Technol. Biotechnol., 2009, 84, 1051–1055.
- 7 S. S. Balula, C. M. Granadeiro, A. D. S. Barbosa, I. C. M. S. Santos and L. Cunha-Silva, *Catal. Today*, 2013, **210**, 142–148.
- 8 S. S. Balula, L. Cunha-Silva, I. C. M. S. Santos, A. C. Estrada, A. C. Fernandes, J. A. S. Cavaleiro, J. Pires, C. Freire and A. M. V. Cavaleiro, *New J. Chem.*, 2013, 37, 2341–2350.
- 9 P. Shringarpure, K. Patel and A. Patel, J. Cluster Sci., 2011, 22, 587–601.
- 10 J. Tang, X. L. Yang, X. W. Zhang, M. Wang and C. D. Wu, *Dalton Trans.*, 2010, **39**, 3396–3399.
- 11 M. T. Reetz and K. Töllner, *Tetrahedron Lett.*, 1995, 36, 9461–9464.
- 12 Q. H. Tang, Q. H. Zhang, H. L. Wu and Y. Wang, *J. Catal.*, 2005, **230**, 384–397.
- 13 C. Chiappe, A. Sanzone and P. J. Dyson, *Green Chem.*, 2011, 13, 1437–1441.
- 14 R. De Paula, M. M. Q. Simoes, M. G. P. M. S. Neves and J. A. S. Cavaleiro, J. Mol. Catal. A: Chem., 2011, 345, 1–11.
- 15 G. Romanowski, J. Mol. Catal. A: Chem., 2013, 368, 137-144.
- 16 S. Shit, U. Yadava, D. Saha and R. Frohlich, J. Coord. Chem., 2013, 66, 66–76.
- 17 S. S. Balula, C. M. Granadeiro, A. D. S. Barbosa, I. C. M. S. Santos and L. Cunha-Silva, *Catal. Today*, 2013, 210, 142–148.
- 18 C. W. Jones, Applications of Hydrogen Peroxide and Derivatives, Royal Society of Chemistry, Cambridge, 1999.
- 19 R. Sheldon, Chem. Commun., 2001, 2399-2407.
- 20 J. Song, Z. Zhang, T. Jiang, S. Hu, W. Li, Y. Xie and B. Han, J. Mol. Catal. A: Chem., 2008, 279, 235–238.
- 21 Z. Zhang, H. Li, Y. R. Liu and Y. H. Ye, Synth. React. Inorg., Met.-Org. Nano-Met. Chem., 2009, **39**, 144-148.
- 22 V. V. Namboodiri, R. S. Varma, E. Sahle-Demessie and U. R. Pillai, *Green Chem.*, 2002, 4, 170–173.

- 23 Y. Z. Voloshin, N. A. Kostromina and R. Krämer, *Clathrochelates: Synthesis, Structure and Properties*, Elsevier Science, Amsterdam, 1st edn, 2002.
- 24 I. I. Creaser, J. M. Harrowfield, A. J. Herlt, A. M. Sargeson, J. Springborg, R. J. Geue and M. R. Snow, *J. Am. Chem. Soc.*, 1977, **99**, 3181–3182.
- 25 F. Pina, M. Maestri, R. Ballardini, Q. G. Mulazzani, M. D'Angelantonio and V. Balzani, *Inorg. Chem.*, 1986, 25, 4249–4252.
- 26 I. I. Creaser, R. J. Geue, J. M. Harrowfield, A. J. Herlt, A. M. Sargeson, M. R. Snow and J. Springborg, *J. Am. Chem. Soc.*, 1982, **104**, 6016–6025.
- 27 V. Houlding, T. Geiger, U. Kolle and M. Gratzel, J. Chem. Soc., Chem. Commun., 1982, 681–683.
- 28 P. A. Lay, A. Mau, W. H. F. Sasse, I. I. Creaser, L. R. Gahan and A. M. Sargeson, *Inorg. Chem.*, 1983, **22**, 2347–2349.
- 29 M. A. R. Scandola, F. Scandola, A. Indelli and V. Balzani, *Inorg. Chim. Acta Lett.*, 1983, **76**, L67–L68.
- 30 F. Pina, Q. G. Mulazzani, M. Venturi, M. Ciano and V. Balzani, *Inorg. Chem.*, 1985, 24, 848–851.
- 31 P. K. B. Palomaki, M. R. Civic and P. H. Dinolfo, ACS Appl. Mater. Interfaces, 2013, 5, 7604–7612.
- 32 N. L. Ritzert, J. Rodriguez-Lopez, C. Tan and H. D. Abruna, *Langmuir*, 2013, **29**, 1683–1694.
- 33 Y. He, D. Gillespie, D. Boda, I. Vlassiouk, R. S. Eisenberg and Z. S. Siwy, *J. Am. Chem. Soc.*, 2009, **131**, 5194–5202.
- 34 E. I. Iwuoha, S. Joseph, Z. Zhang, M. R. Smyth, U. Fuhr and P. R. O. de Montellano, *J. Pharm. Biomed. Anal.*, 1998, 17, 1101–1110.
- 35 C. Ley, H. Schewe, F. W. Stroehle, A. J. Ruff, U. Schwaneberg,
 J. Schrader and D. Holtmann, *J. Mol. Catal. B: Enzym.*, 2013,
 92, 71–78.
- 36 J. Nazor and U. Schwaneberg, *ChemBioChem*, 2006, 7, 638–644.
- 37 U. Schwaneberg, D. Appel, J. Schmitt and R. D. Schmid, *J. Biotechnol.*, 2000, 84, 249–257.
- 38 L. R. Gahan, P. C. Healy and G. J. Patch, J. Chem. Educ., 1989, 66, 445.
- 39 T. Kottke and D. Stalke, J. Appl. Crystallogr., 1993, 26, 615–619.
- 40 APEX2, *Data Collection Software Version 2.1-RC13*, Bruker AXS, Delft, The Netherlands, 2006.
- 41 Cryopad, *Remote monitoring and control, Version 1.451*, Oxford Cryosystems, Oxford, United Kingdom, 2006.
- 42 SAINT+, Data Integration Engine v. 7.23a ©, Bruker AXS, Madison, Wisconsin, USA, 1997–2005.
- 43 G. M. Sheldrick, *SADABS v.2.01, Bruker/Siemens Area Detector Absorption Correction Program*, Bruker AXS, Madison, Wisconsin, USA, 1998.
- 44 G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, 1997.
- 45 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, 64, 112–122.

- 46 G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, 1997.
- 47 A. L. Spek, Acta Crystallogr., Sect. A: Found. Crystallogr., 1990, 46, C34.
- 48 A. L. Spek, J. Appl. Crystallogr., 2003, 36, 7-13.
- 49 P. van der Sluis and A. L. Spek, Acta Crystallogr., Sect. A: Found. Crystallogr., 1990, 46, 194–201.
- 50 J. F. Endicott, G. R. Brubaker, T. Ramasami, K. Kumar, K. Dwarakanath, J. Cassel and D. Johnson, *Inorg. Chem.*, 1983, 22, 3754–3762.
- 51 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds: Theory and applications in inorganic chemistry*, John Wiley, 1997.
- 52 F. H. Allen, Acta Crystallogr., Sect. B: Struct. Sci., 2002, 58, 380-388.
- 53 F. H. Allen and W. D. S. Motherwell, *Acta Crystallogr., Sect. B:* Struct. Sci., 2002, 58, 407–422.
- 54 M. Mikami, M. Konno and Y. Saito, *Acta Crystallogr., Sect. B:* Struct. Crystallogr. Cryst. Chem., 1979, **35**, 3096–3098.
- 55 M. P. Suh, W. Shin, D. S. Kim and S. S. Kim, *Inorg. Chem.*, 1984, 23, 618–620.
- 56 A. Bacchi, F. Ferranti and G. Pelizzi, Acta Crystallogr., Sect. C: Cryst. Struct. Commun., 1993, 49, 1885–1892.
- 57 A. Bacchi, F. Ferranti and G. Pelizzi, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1993, **49**, 1163–1169.
- 58 A. Bacchi, F. Ferranti and G. Pelizzi, Acta Crystallogr., Sect. C: Cryst. Struct. Commun., 1996, 52, 1624–1627.
- 59 R. Castro, L. A. Godinez, C. M. Criss, S. G. Bott and A. E. Kaifer, *Chem. Commun.*, 1997, 935–936.
- 60 A. Schonleber, S. van Smaalen and F. K. Larsen, Acta Crystallogr., Sect. C: Cryst. Struct. Commun., 2010, 66, M107–M109.
- V. Skripacheva, V. Burilov, A. Mustafina, O. Kataeva, M. Gruner, V. Yanilkin, A. Stepanov, V. Syakaev, R. Zairov, S. Soloveva, W. Habicher and A. Konovalov, *J. Inclusion Phenom. Macrocyclic Chem.*, 2011, 69, 191–199.
- 62 L. L. Liu, C. C. Chen, X. F. Hu, T. Mohamood, W. H. Ma, J. Lin and J. C. Zhao, *New J. Chem.*, 2008, **32**, 283–289.
- 63 L. Shu and Y. Shi, J. Org. Chem., 2000, 65, 8807-8810.
- 64 Z. F. Li, S. J. Wu, Y. Y. Ma, H. Liu, J. Hu, L. L. Liu, Q. S. Huo, J. Q. Guan and Q. B. Kan, *Transition Met. Chem.*, 2013, 38, 243–251.
- 65 J. L. Hu, K. X. Li, W. Li, F. Y. Ma and Y. H. Guo, *Appl. Catal.*, *A*, 2009, **364**, 211–220.
- 66 P. A. Shringarpure and A. Patel, *React. Kinet., Mech. Catal.*, 2011, **103**, 165–180.
- 67 M. R. Maurya, P. Saini, C. Haldar and F. Avecilla, *Polyhedron*, 2012, **31**, 710–720.
- 68 F. Marchetti, C. Pettinari, C. Di Nicola, R. Pettinari,
 A. Crispini, M. Crucianelli and A. Di Giuseppe, *Appl. Catal.*,
 A, 2010, 378, 211–220.
- 69 C. M. Granadeiro, P. Silva, V. K. Saini, F. A. A. Paz, J. Pires, L. Cunha-Silva and S. S. Balula, *Catal. Today*, 2013, 218, 35–42.