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The sulfoxidation reaction catalyzed by $CoBr_2$ complexes, under the magnifying glass of green parameters

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Nickel (II) bromide ($NiBr_2$) (PubChem CID: 278492)
iron (III) nitrate ($Fe(NO_3)_3$) (PubChem CID: 25251)
4-(methylthio)acetophenone, **1** (PubChem CID: 74501)
4-(methylthio)benzaldehyde **2** (PubChem CID: 76985)
4-(methylthio)bromobenzene **3** (PubChem CID: 66037)
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ABSTRACT

Different cobalt (II) and nickel (II) species were used as catalysts in sulfoxidation reactions giving excellent yields and high chemoselectivity. Among the cobalt (II) species, both γ-cyclodextrin complexes synthesized in ethyl acetate or dichloromethane solvents were very good catalysts, while γCDNiBr_2 synthesized in ethyl acetate was the best of Ni (II) species. Sulfoxidation takes place with high chemoselectivity in the presence of other groups such as aldehyde. Good results were obtained when these reactions were analyzed using green chemistry metrics. Techniques as FT-IR, UV–vis Diffuse Reflectance, colorimetry, TGA, flame atomic absorption, potentiometric halide titration, and elemental analysis were used to characterize novel complexes. The change of solvent in the synthesis of complexes produces positive effects in holistic green metrics.

1. Introduction

Organosulfur compounds, such as sulfoxides, are very important synthetic intermediates in organic chemistry [1,2]. These compounds are valuable in the preparation of pharmaceutically and biologically relevant materials [3,4,5]. In pharmaceutical research and production, sulfoxidation is one of the oxidation reactions most commonly found, achieved with a large variety of reagents, catalysts and oxidants [6,7]. Sulfoxidation reaction is often difficult to carry out in organic synthesis since other functional groups can be oxidized simultaneously [8]. Furthermore, it is important that catalysts or oxidizing conditions have a high selectivity to yield sulfoxides, as these can undergo over-oxidation to sulfones [9,10,11]. Chemoselective transformations are of central importance [12], especially when several different functional groups are present in a molecule as in esomeprazole [13], a sulfoxide-containing drug. It is known that oxidation reactions account for only 4% of the reactions carried out in the pharmaceutical industry [14]. However, one of the reasons why oxidation reactions are not used more frequently used is due to the fact that the available procedures are not clean or safe enough [5]. In 2006, ACS GCI pharmaceutical Roundtable members identified oxidation/epoxidation reactions as an area requiring focused research to advance the principles of green chemistry and their application in the pharmaceutical industry [15].

In view of continuous interest in the development of synthetic methods for the selective conversion of sulfides into sulfoxides [16,17,18,19] and, in the general, in the oxidation of sulfides [20,21], we are seeking the development of reaction methodologies to achieve chemoselective sulfoxidation reactions.

From our studies, it was concluded that iron salts made up an excellent catalytic system for the oxidation of sulfides to sulfoxides

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[22,23,24,25]. In addition, we have reported the synthesis, characterization and catalytic activity of several cyclodextrins-$FeBr_3$ (CD-Fe) complexes, these also having a very good catalytic activity in sulfoxidation reactions [26,27,28].

Cobalt and nickel compounds [29,30] are very important in several scientific areas, such as materials design [31,32,33], biological processes [34,35,36], catalysis [37,38], and organic synthesis [39,40,41]. The structure elucidation of cobalt or nickel complexes [42] largely benefits all these fields, since the mechanisms of the reactions where they could be used are better understood when you have detailed structural information.

Besides, cyclodextrins (CDs) have been extensively used as hosts in the formation of divers inclusion complexes with organic [43], organometallic [44,45,46] and inorganic guests [47,48,49]. CDs are cyclic oligomers of D-glucose, bonded by α-1-4 linkages. They have a toroidal structure similar to a truncated cone. Their interior behave as a hydrophobic cavity, while the 2, 3 and 6 hydroxyl groups of the glucose units are located at the edges of the truncated cone, defining the hydrophilic zones of the oligomer [50]. The inclusion complexes have been studied, in most cases, using the conventional techniques for solution-state or X-Ray diffraction for crystalline solids [51,52]. The metal-based CD complex subject was newly reviewed [53,54]. In the literature, most complexes characterized were prepared in basic solution [55]; yet, there are a few synthesized in deionized water but not in basic solution [56], and toluene was used in the synthesis of one complex [57]. Specifically, natural γ-cyclodextrin (γ-CD) is the less commonly used CD in industrial products and it is about 5% of global CD production. Physicochemical properties are well known, natural γ-CD being the biggest and most soluble of all CD natives [58].

In the previous paper, we have reported studies over transition metal salt-CD complexes both their synthesis in different organic solvents [26], as their application over sulfoxidation reactions as heterogeneous catalysts [28]. The main advantages of this synthesis methodology are its simplicity, the agreement with the aims of the Green Chemistry Principles, and quantitative yield [59]. Moreover, it should be noted that these complexes can be stored without any special care because they are very stable. It should be noted that the complex βCD/$FeBr_3$, prepared in 1/1 molar ratio and in dichloromethane (DCM) as synthesis solvent, was a better catalyst, for the oxidation of methylphenylsulfide, than complexes prepared with higher βCD/Fe molar ratio in other solvents.

These complexes cannot be characterized by X-Ray diffraction study of monocrystals since they are amorphous powders. Nevertheless, our group characterized $CDCuX_2$ complexes of similar nature using many techniques and analyzing obtained data in an integrated manner [60].

Green Chemistry was introduced with the aim of overcoming health and environmental problems at the source by developing cleaner chemical processes for chemical industry through the design of innovative and environmentally benign chemical reactions [61,62,63]. Diverse green metrics have also been approached [64,65,66,67] and used in Green evaluations over different reactions [68,69,70]. We have reported green metric parameters in previous studies with very good results (see refs [25] and [56]).

Thus, we report here that substrates such as 4-(methylthio)acetophenone, **1;** 4-(methylthio)benzaldehyde **2;** 4-(methylthio)bromobenzene **3** and (methylthio)benzene **4** are oxidized with very high chemoselectivity and in excellent yields (Scheme 1). It should be noted that highly oxidizable function such as aldehyde remains unaltered under the reaction conditions used. The sulfoxidation reactions have been catalyzed by cobalt bromide and γ-cyclodextrin complex synthesized in dichloromethane (DCM) [$\gamma CDCoBr_{2(DCM)}$] or in ethyl acetate (EtAc) [$\gamma CDCoBr_{2(EtAc)}$] or by nickel bromide and γ-cyclodextrin complex synthesized in DCM [$\gamma CDNiBr_{2(DCM)}$] or in EtAc [$\gamma CDNiBr_{2(EtAc)}$] presented in this paper.

Finally, all results have been analyzed under the magnifying glass of green parameters.

2. Experimental

2.1. Metal complexes

2.1.1. Synthesis of metal complexes

Complexes were prepared as previously reported for $FeBr_3$ [26]. For example, it stirred for 30 min 1 mmol of Co^{2+} salt in 10 mL of dichloromethane or ethyl acetate (colouration could be seen in both solvents); then solid cyclodextrin was added in 1:1 molar ratio. This heterogeneous mixture was stirred for 24 h, later the solid was filtered, washed with DCM or EtAc (3 × 5 mL of the same solvent) and dried under air. During complex formation, colouration of the white CD powder in contrast to organic solvent decolouration could be observed. Of the total mass at the start used, it was recovered between 98% and 100%. When dichloromethane was used, decolouration was complete; however, in the case of ethyl acetate, light colouration was found (it corresponds approximately to < 1% initial amount of salt; quantification was performed by UV–vis spectroscopy).

2.1.2. Stoichiometry determination

The combination of the data provided by the different analysis is need to stoichiometry determination of the complex. We could determine the percentages of C, H, Br, O, N and Co or Ni in the sample, from the data resulting from elemental analysis, potentiometric halogen titration and flame atomic absorption. The procedure is similar to that reported in a previous paper [60], with a general formula equal to $A(C_{48}H_{80}O_{40}) \cdot B(MBr_2) \cdot D(H_2O)$. Only two changes were introduced: D values from 1 to 20 in 0.5 intervals were used and % *Br* will be determined as follows (Eq. (1)):

$$\%Br = \frac{B\ x\ 79.9}{MW}\ x\ 100 \quad (1)$$

We compared the experimental data with the 195 theoretical percent compositions obtained.

2.1.3. Elemental analysis

To realize the measurements, it was used a combustion-gas chromatography Perkin Elmer 2400 Series II CHNS. A standard cystine sample was used to calibrate (Perkin Elmer, 99.99%). All solid complexes were analyzed in triplicate.

2.1.4. Flame atomic absorption

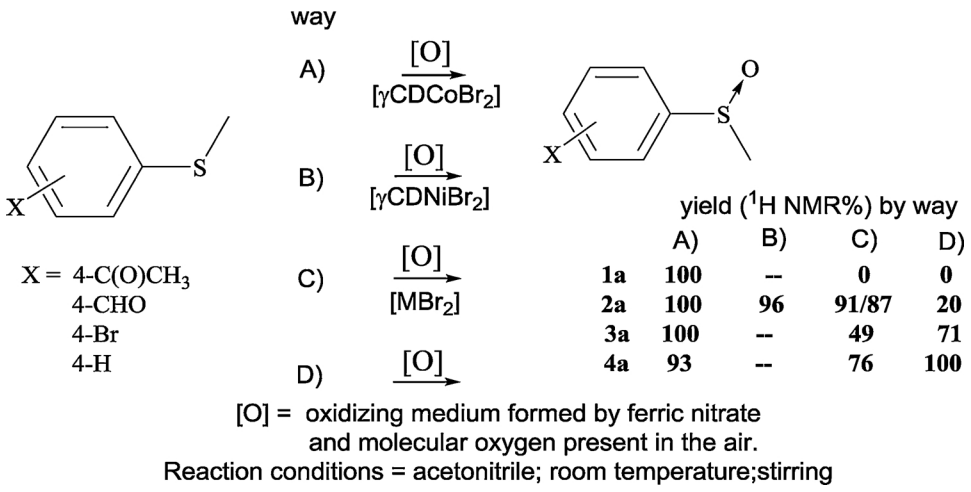
To realize the measurements, it was used a Perkin Elmer Mod. 3110; nickel complexes were analyzed with air-acetylene flame and cobalt complexes were analyzed with nitrous oxide-acetylene flame. The preparation of sample consists of dissolving about 10 mg of complex with 2 mL of concentrated HCl and 2 mL of concentrated HNO_3 for 1 h. Later, the solution was completed to 5 mL with milliQ water. All samples were analyzed in triplicate.

2.1.5. Potentiometric halide titration

Potentiometric titration of halide ions was performed with $AgNO_3$ on a pHmeter (model Orion 420A) equipped with a silver ($Ag+$)/sulfide (S^{2-}) selective electrode. The preparation of the sample involved the dilution of approximately 10 mg of complex in 2 mL of milliQ water. Afterwards, the solution was transferred to a 25 mL flask. Then, 10 mL of this solution were taken in a becker, and 5 drops of HNO_3 and 5 mL of miliQ water were added. At last, the solution obtained was titrated with a solution of $AgNO_3$ with (0.097 ± 0.002) M concentration. All titrations were carried out at least three times and all results showed good agreement with each other. The average value was used.

2.1.6. Thermal gravimetric analysis

To realize the TGA studies and analyses, it was used a thermogravimetric analyzer equipment Hi-Res Modulated TGA 2950. As from experimental thermograms it were calculated derivative



Scheme 1. xxx.

thermogravimetric analyses (DTGA). All solid complexes were measured from 25 °C to 500 °C with a heating rate of 10 °C/min, in N_2 atmosphere.

2.1.7. UV–vis diffuse reflectance

BLACK-Comet StellarNet Inc spectrometer equipment was used with UV–vis optical fibbers suitable for measuring diffuse reflectance and colorimetry. Spectra were acquired in the range of 200 to 1050 nm (50000–12500 cm^{-1}). Each solid complex was measured 10 times and data were averaged. Kubelka-Munk equation was using to parameterized the reflectance (R) data obtained [71] (Eq. (2)) and PeakFit Software was used to deconvoluted the spectra.

$$F(R) = \frac{(1-R)^2}{2R} \tag{2}$$

Colorimetric measurements were been using SpectraWiz® Spectroscopy Software, and with D65 illuminant were obtained CIELab parameters a, b and L, also averaging 10 measurements [72][1]. ΔE, the color difference,[73] was computed as (Eq. (3))

$$\Delta E = [(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2]^{1/2} \tag{3}$$

2.1.8. FT-IR

To realize the IR spectra, it was used a Nicolet 5SC spectrophotometer. It was used KBr pellets containing 1% of solid complex. Spectra were acquired at a resolution of 2 cm^{-1}. The procedure is the same as that followed in a previous paper (see ref [60]). The pure CD and the complex presented the main spectral differences in the regions of 3300–2900 cm^{-1} (stretching of primary and secondary OH) and 1600–1680 cm^{-1} (water molecules in the cavity of the CD). Other changes, less important, were observed to signal of CH bending and OH in plane bending (1225–1240 cm^{-1}), CO stretching of the secondary OH (1080–1120 cm^{-1}), CO stretching of the primary OH (1035–1060 cm^{-1}) and ring vibrations (920–960 cm^{-1}) [74].

When a bathochromic shift in the maximum of the signal corresponding to the stretching of OH is observed, can be due that hydrogen bonds between CD molecules have weakened. This sould so because to interactions between CD molecule with the host [75]. The signal at 1640 cm^{-1} was analysed the same way. The maximum values of these signals were subtracted from those of the native CD (Eq. (4)). Differences smaller than 10 cm^{-1} were not considered [76].

$$\nu_{Complex} - \nu_{CD} = \Delta\nu \tag{4}$$

2.2. Sulfoxidation reaction

^{1}H NMR spectra were carried out in a 400 MHz Bruker Avance II spectrometer. The solvents used were analytical-grade commercially available samples used as received. Substrates 4-(methylthio)benzaldehyde **1**; 4-(methylthio)acetophenone, **2;** 4-(methylthio)bromobenzene **3** and (methylthio)benzene **4** were obtained from commercial suppliers. Products were characterized by ^{1}H NMR spectra and found to be identical to authentic samples. Spectra of compounds are available in Supplementary Data.

2.2.1. General procedure

All reactions were carried out in an open reaction tube, with magnetic stirring at room temperature. The molar ratios substrate: catalyst: nitrate were 1.00: 0.10: 0.30. In a typical procedure, the substrate (1 mmol) was dissolved in acetonitrile (3.5 mL) and the cobalt complex (0.10 mmol) and the iron (III) nitrate (0.30 mmol) were added. The reaction time was 5 hours. The reaction medium with cyclodextrin complexes was heterogeneous since complexes are solid, not soluble in this system. Once the reaction was over, the solution was filtered and the solid washed several times with dichloromethane or ethyl acetate in agreement with solvent synthesis of the complex used. After filtration, products were purified by column chromatography on silica gel 60 (70–230 mesh ASTM), the mobile phase used was 1:1 ethyl ether: chloroform mixture. The residue was analyzed by different chromatographic and spectroscopic methods. All reactions were conducted in duplicate. In no case were sulfones detected. The percent enantiomeric excess (% ee) was calculated as % ee = $\{([\alpha]_{observed}/[\alpha])x100\}$, in each case and when possible, from maximum optical rotation of bibliography.

The parameter turnover number (TON) (Eq. (5)) and turnover frequency (TOF) (Eq. (6)) were calculated as follows:

$$TON = \frac{product\ \ mol}{catalyst\ \ mol} \tag{5}$$

$$TOF = \frac{product\ \ mol}{catalyst\ \ mol} x\ h^{-1} \tag{6}$$

2.3. Green metric calculations

The green metrics were calculated using the procedures reported in

[1] The CIELab is considered the most accurate colour model and has a large colour gamut. This colorimetric method was used as recommended by the Commission Internationale de l' Eclairage. The **a** axis extends from red (+**a**) to green (-**a**) and the **b** axis from yellow (+**b**) to blue (-**b**); lightness (**L**) axis is perpendicular to (**a**) and (**b**) plane with a value of 0 for black and 100 for white.

the literature. They are defined as follows [77]:

$$\text{Mass intensity (MI)} = \frac{\text{Total mass used in a process or process step (g)}}{\text{Mass of product (g)}}$$

$$\text{Reaction mass efficiency (RME)} = \frac{\sum \text{mass of product}}{\sum \text{mass of reactants}} \text{x100}$$

$$\text{Atom economy (AE)} = \frac{\text{molecular weight of product}}{\sum \text{molecular weight of reactants}}$$

EcoScale [78] and Green Start (*GS*) [79,80] were calculated using procedures and critical evaluation [66] reported in the literature.

A theoretical example of a typical calculation follows: 4-(Methylthio)benzaldehyde (0.1522 g, 1 mmol, FW 152.21) reacts with iron (III) nitrate nonahydrate (0.1212 g, 0.30 mmol, FW 404.00) and molecular oxygen (0.016 g, 0.5 mmol, FW 32.00) in the presence of $\gamma CDCoBr_{2(EtAc)}$ (0.1516 g, 0.10 mmol, FW 1515.87) in acetonitrile (3.5 mL, 2.751 g) to give 4-(methylsulfinyl)benzaldehyde (FW 168.21) isolated in 100% yield (1.00 mmol, 0.1682 g). TON = 10; TOF = 2 h^{-1}.

The amount of catalyst was not used in the calculations since it is recoverable by filtration and can be reused. For *AE*, reagents in catalytic quantities and catalysts are not considered in the calculation. The score of principles in *GS* are listed in supplementary data. Principles P4 and P11 of *GS* are not assessed here as they correspond to an industrial evaluation.

Mass Intensity = [(0.1522 + 0.1212 + 0.016 + 2.751)/0.1682] = 18.1

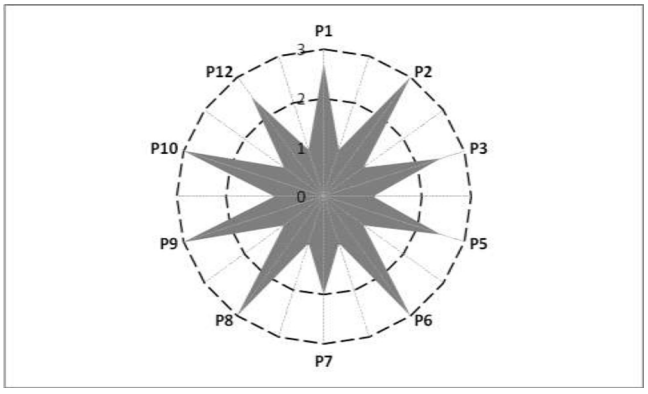
Reaction Mass Efficiency = [0.1682/(0.1522 + 0.1212 + 0.016)] x 100 = 58.1%

Atom Economy = [168.21/(152.21 + 32.00)] x 100 = 91.3%

EcoScale: 100 − Σ penalty points = 81

Parameters of Quality	Penalty points assigned
Yield	0
Price of reaction components	3
Safety	5
Temperature/Time (Energy)	1
Technical Setup	0
Work-Up/Purification	10
Σ penalty points	19

Green Start: *GSAI* % (Green Star Area Index) = 86.0



3. Results and discussion

In this section, we present and discuss the synthesis and characterization of the Co and Ni complexes, the results obtained in the sulfoxidation reaction using the complexes as catalysts and Green Chemistry parameters of all synthesis performed.

Organic solvents used in the synthetic process of complexes were dichloromethane or ethyl acetate and no water was used. Thus, it is important to note that Co or Ni salts could not be denatured or hydrolysed [81].

In agreement with our previous paper [60], it should be considered that complexes are made up from $CoBr_2$ or $NiBr_2$ and cyclodextrin (macrocyclic oligosaccharide); therefore, we expected coordination between the macrocycle and the metallic centre. In addition, the bromides (counterions) may also form part of the metal coordination sphere. These complexes were synthesized in two solvents, dichloromethane as in our previous studies and ethyl acetate as a very good alternative of green solvent.

Results obtained from different techniques were analysed in an integrated way, in order to gather information about the physical chemical properties and structure of the complexes, as described below. A comprehensive description of the procedure is shown, as an example, for γCD and $CoBr_2$ complex ($\gamma CDCoBr_2$) synthesized in DCM. The other complexes discussed in this paper were analysed in a similar way. (see Supplementary Data, Figs. 1S–6S and Table 1S).

With the integrated analysis of obtained results in elemental analysis (EA), flame atomic absorption and potentiometric titration, it was determined that, for $\gamma CDCoBr_2$, the molecular formula is $DH_2O \cdot (C_{48}H_{80}O_{40}) \cdot (CoBr_2)$. Thus, there is a 1:1 relationship between γ-CD and $CoBr_2$. The value of D is 4.9, when it is calculated from TGA analysis, while EA data yield a value of 4.0 (see Supplementary Data, Table 1S for native γ-CD and other complexes).

3.1. Thermogravimetric analysis

The TGA and DTGA analysis of γCD native agree with data reported [82], and they are considerably different with from those of the complex (see Fig. 1).

It can be observed in the DTGA plots that around 53 °C a peak appears in both compounds. Also γCD has a small peak at 116 °C that appears at 130 °C in the complex. These peaks are attributed, in general, to the release of hydration water molecules (hwm)[83]. However, the fact that the elimination of some water molecules takes place at high temperature has been considered as evidence that they are coordinated

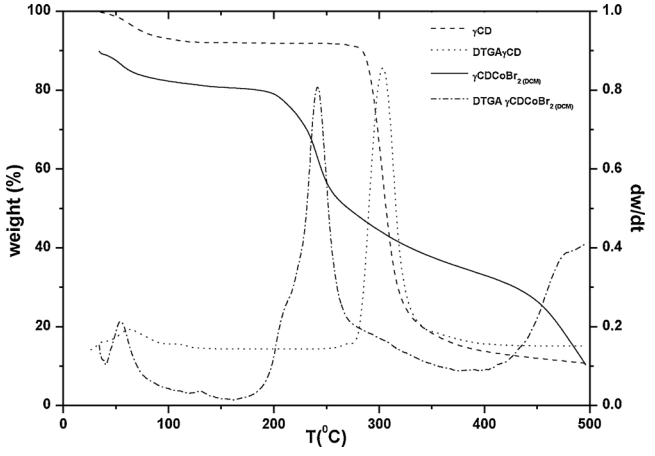


Fig. 1. TGA and DTGA of $\gamma CDCoBr_{2(DCM)}$ complex (solid lines) and γCD (dotted line).

Table 1
Thermal analysis results.

Native or Complex γCD[a]	T_{hwm}[b] (°C)	T_{dec}[c] (°C)	T_d 50%[d] (°C)	$\%m_r$[e]	$T_{DTGApeaks}$[d] (°C)
γCD*	62 and 109	267	306	10.65	53 - 116 - 295
γCD**	50 and 97	274	306	10.54	63 - 105 - 303
$\gamma CDCoBr_2$ (DCM)*	54	206	329	20.23	54 - 130 - 242
$\gamma CDCoBr_2$ (EtAc)**	32 and 64	187	297	10.66	33 - 65 - 150 - 226 - 434
$\gamma CDNiBr_2$ (DCM)*	48 and 112	187	356	30.94	60 - 108 - 213 - 239
$\gamma CDNiBr_2$ (EtAc)**	71	180	310	6.49	71 - 215 - 328 - 384

[d] $T_{DTGApeaks}$: maximum values in differential thermogravimetric analysis (DTGA) plots

[a] Two batches of CD were used; the complexes synthesized with each of them are indicated by * or **.

[b] T_{hwm}: Temperature of mass loss corresponding to hydration water molecules.

[c] T_{dec}: Initial temperature of macrocyclic decomposition step.

[d] T_d50%: Decomposition temperature of 50% of the initial mass.

[e] $\%m_r$: Percentage of remaining mass.

to the metal centre [84]. On the other hand, there is no regularity in the behaviour of the different complexes above this temperature (see Table 1).

The decomposition profiles of the complexes is also very different from that of native CD. While the native CD shows only one clear thermal transition at 306 °C, the macrocycle degradation in $\gamma CDCoBr_2$ is carried out in several steps. Metallic centre is able to coordinate the smaller fragments generated from initial carbohydrates, so they are eliminated at different temperatures [85]. All complexes showed a similar behaviour (see Table 1 and Supplementary Data, Figs. 1S, 3S, 5S).

From different parameters, i.e., the initial temperature of macrocyclic decomposition step (T_{dec}), decomposition temperature of 50% of the initial mass (T_d50%), and the temperature value of the transitions in the DTGA, it can be discussed the thermal stability of the complexes. As shown in Table 1, in all cases, the initiation of the decomposition event is carried out at a temperature lower than that of the γCD since the complexes synthesized in EtAc show lower temperature. On the other hand, the T_d50% values of the complexes are higher than the native CD, except for $\gamma CDCoBr_{2(EtAc)}$. Hence, it can be concluded that the presence of Co or Ni salts accelerates the thermal decomposition of the macrocycle and the solvent used in the synthesis could have some participation in the stability of solid complexes.

Also the remaining mass ($\%m_r$) was analysed. This parameter can also shed light into the complex structure (see Table 1). In two complexes synthesized in DCM, the remaining mass was higher than in the γCD, whereas that in those synthesized in EtAc the remaining mass was equal to or minor than native CD. Since no solvent remained in the solid complexes, these results might indicate that in complexes synthesized in DCM the coordination of the oxygens of the host with the metal is stronger than that in complexes synthesized in EtAc. This may be due to interaction and/or competition of oxygen atoms of EtAc by the metallic centre during the synthetic process.

When we compared the thermal behaviour of the complexes, we observed that it was different from that of other complexes reported in the literature [86], while this behaviour has some likeness with our previous report on Cu complexes [60]. The dissimilar synthetic processes, that could lead to compounds with different structures, can be responsible of these discrepancies [56].

3.2. UV-vis diffuse reflectance

It is called Δ_0 to the difference in energy generated by the split of the *d* orbital into high and low energy orbitals when transition metal is attach with ligands to form a coordination complex; it is characteristic of both metal and ligand. Δ_0 values and ligand-to-metal charge transfer (LMCT) were analyzed by UV–vis diffuse reflectance measurements [87].

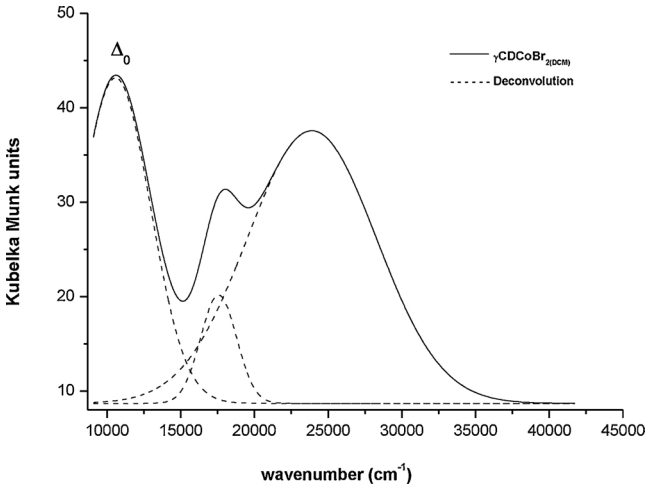


Fig. 2. UV–vis Diffuse Reflectance (DR) of $\gamma CDCoBr_{2(DCM)}$. Dashed lines show the deconvolution of the bands.

Since Co^{2+} has a d^7 configuration, three transitions should be expected in the Uv–vis of the complex [88]. As these three bands are close in wavenumber values, it is necessary the deconvolution of the spectra with three Gaussians. The UV–vis diffuse reflectance of the $\gamma CDCoBr_{2(DCM)}$ powder is showed into Fig. 2, as well as the bands resulting from the deconvolution of the spectra (the maximum values are listed in Table 2).

Δ_o is determined from the maximum of the highest intensity signal with A value of 10586 cm^{-1}, consistent with a distorted octahedral geometry. The observed bands have been assigned to the transition in agreement with the bibliography. Complexes presented here showed no ligand-to-metal charge transfer (LMCT) transition (see also spectra of other complexes, Figs. 2S, 4S, 6S and Table 2) [88,89].

It was not possible to determine a preferred position for the metal centre being that the only coordinating atoms in CDs are the primary or secondary OH groups (at the rim) and the glycosidic oxygens (oxygens located in the cavity). Insomuch as its mobility is constrained in a confined space and the interaction may be more efficient. Nevertheless, it may be assumed that a higher orbital overlap is mostly favoured when the guest is more included [90].

The bands in the UV–vis are broad with a considerable value of area, it suggest that several isomers of the complex may be present in the powder. γ-CD is a big ligand with multiple coordinating atoms, then it can be possible than complexes with different geometry are be present. For example, three different ligands (oxygen from water molecules, halide, oxygens form γ-CD) with identical stoichiometry, may be in a distinct coordination position (equatorial, axial or both) and result in Co^{2+} atoms with different environments, which may cause a broadening in the UV–vis bands. All these was discussed in a previous paper with Cu^{2+} as metallic centre [60].

So all complexes show a distorted octahedral geometry as it can be inferred from data showed in Table 2.

In Addition, we compared the Δ_o values obtained for complexes of γCD synthesized in different solvents, and it can be said that there are differences in transitions $^4T_{1g} \rightarrow {}^4T_{1g(4P)}$ for Co complexes and $^3A_{2g} \rightarrow {}^3T_{1g(3F)}$ and $^3A_{2g} \rightarrow {}^3T_{1g(3P)}$ for Ni complexes, in $\gamma CDNiBr_{2(DCM)}$ the last transition is missing.

The colorimetric measurements are be used in scientific fields such as synthesis and characterization of materials [91] or nanopigments [92] among others; however, when organometallic compounds are

Table 2
Spectroscopic data of the complexes.

Complex	$_{\Delta 0}$ (cm^{-1}) ; transition			Color (CIE L*a*b*)			
	$^4T_{1g} \rightarrow {}^4T_{2g(4F)}$	$^4T_{1g} \rightarrow {}^4A_{2g(4F)}$	$^4T_{1g} \rightarrow {}^4T_{1g(4P)}$	L	a	b	ΔE
γCDCoBr$_{2(DCM)}$	10586	17574	23899	82.32	-2.91	-14.34	5.72
γCDCoBr$_{2(EtAc)}$	10722	17431	25285	77.15	-5.35	-13.78	
	$^3A_{2g} \rightarrow {}^3T_{2g(3F)}$	$^3A_{2g} \rightarrow {}^3T_{1g(3F)}$	$^3A_{2g} \rightarrow {}^3T_{1g(3P)}$				
γCDNiBr$_{2(DCM)}$	9732	18749	–	93.35	-6.97	11.12	7.64
γCDNiBr$_{2(EtAc)}$	9996	17464	27283	95.36	-8.62	18.30	

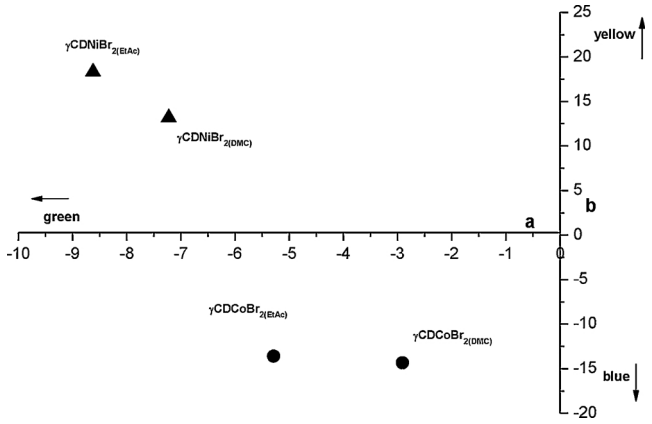


Fig. 3. a* and b* parameters of the CIELab space of the different complexes.

characterized, this technique is rarely used [93]. The same happens with the CIE L*a*b* parameters, these have been used to characterize of ceramic glazes [94]; to monitor oxidation in raw meat [95]; or to find relationships between solvatochromism and chromaticity [96] but seldom for organometallic complexes.

The colorimetric data of the complexes are summarized in Table 2. Whereas that in Fig. 3 are showed the a* b* chromaticity diagram of the CIELAB color space. For parameter a, the negative direction of the horizontal axis indicates a green component; the positive direction indicates a red component. For parameter b, the positive direction of the vertical axis indicates a yellow component while the negative indicates a blue one. On the other hand, the chromaticity is obtained of the absolute value of the distance from the origin of coordinates to the colorimetric value. This parameter expresses the intensity of the colour, the greater the distance, the higher the chromaticity (Fig. 4).

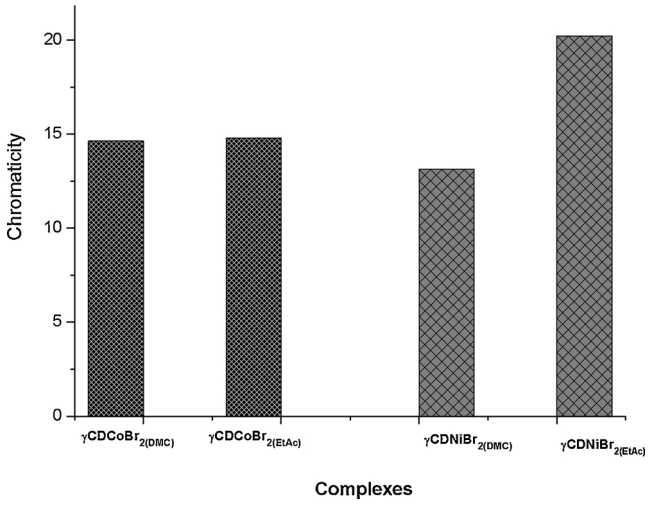


Fig. 4. Chromaticity value of all the compounds synthesized.

The analysis of the data shows that colorimetric values are highly dependent on the metallic centre. From the differences in the L, a* and b* parameters, is possible say that the colorimetric values can be used as a fingerprint for these CD complexes. This allows the identification of each one by a simple procedure. Looking at the L, a* and b* values for each Co complexes in Table 2, it can be determined that the complexes do not match in colour. These values show that γCDCoBr$_{2(DCM)}$ is lighter, less green, and more blue than γCDCoBr$_{2(EtAc)}$. If we put the values of $\Delta L^* = +5.17$, $\Delta a^* = -2.44$, and $\Delta b^* = -0.56$ into the color difference equation, it can be determined that the total colour difference between the two complexes is 5.72. The same analysis can be made for Ni complexes. It is remarkable that the highest absolute values of the CIELab parameters were obtained in Ni complexes.

3.3. IR spectroscopy

Also, we analysed IR spectra. For this, the regions of 3300–2900 cm^{-1}, corresponding to OH of the γ-CD (1st and 2nd OH_{rim}) and 1600–1680 cm^{-1} corresponding to water molecules present in the cavity of the γ-CD (H_2O_{cavity}) have been chosen to discuss.

When the differences in FT-IR spectra are considered (Table 3), it may be observed that only the OH signal is significantly modified. But this fact occurs with a different relative magnitude. It shows than metallic centre interacts with the OH at the rims of the CD, altering the formation of inter and/or intramolecular H bond. However, no differences were observed in the signal of H_2O from the cavity were observed, evidencing that the metal salt does not present a certain degree of inclusion. In addition, the modification in OH signal produced by Ni complexes was lower than that in Co complexes.

3.4. Sulfoxidation reaction

On the basis of our previous studies, we chose four sulfides with different reactivity in agree with Hammett relation; these values are 4-(methylthio)acetophenone, **1,** $\sigma = +0.50$; 4-(methylthio)benzaldehyde **2,** $\sigma = +0.42$; 4-(methylthio)bromobenzene **3,** $\sigma = +0.23$ and (methylthio)benzene **4,** $\sigma = 0.00$ [97]; the amount of co-oxidant was also increased from 0.1 to 0.3 mmol with respect to 1 mmol substrate. The objective of these changes was to search enantio and chemoselectivity conditions on the base of a previous study (see ref. [23]). On the other hand, the use as catalysts of complexes of γCD synthesized in different

Table 3
Differences in the FT-IR bands analysed for all the compounds synthesized.

Native or Complex γCD[a]	OH (cm^{-1})	$_{\Delta 0}$ (cm^{-1})	H_2O (cm^{-1})	$_{\Delta 0}$ (cm^{-1})
γCD*	3384	–	1646	–
γCDCoBr$_{2(DCM)}$*	3364	-20	1643	-3
γCDNiBr$_{2(DCM)}$*	3380	-4	1644	-2
γCD**	3396	–	1647	–
γCDCoBr$_{2(EtAc)}$**	3370	-26	1643	-3
γCDNiBr$_{2(EtAc)}$**	3371	-25	1643	-4

[a] Two batches of CD were used. The complexes synthesized with each of them are indicated by * or **.

Table 4
Oxidation reaction of 4-(methylthio)acetophenone to 4-(methylsulfinyl) acetophenone with γCDCoBr$_2$ complexes or CoBr$_2$ as catalysts.[a]

Entry	Catalyst[b]	Substrate[c]	Yield[c] (%)[d] [polarimetry][e]	TON	TOF
1	–	100	–	–	–
2	CoBr$_2$[f]	100	–	–	–
3	γCDCoBr$_{2(DCM)}$[f]	100	–	–	–
4	γCDCoBr$_{2(EtAc)}$[f]	100	–	–	–
5	CoBr$_2$	100	–	–	–
6	γCDCoBr$_{2(DCM)}$ (10.2% cat)[g]	–	100 (76.7) [-0.90 (1.00)[h]]	7.50	1.50
7	γCDCoBr$_{2(EtAc)}$ (10.1% cat)[g]	–	100 (79.1) [-0.33 (0.36)[h]]	7.82	1.56

[a] Solvent acetonitrile, co-oxidant Fe(NO$_3$)$_3$·9 H$_2$O, ratio substrate: catalyst: co-oxidant 1.00: 0.10: 0.30 mol, at room temperature with stirring, under air, reaction time 5 h.
[b] Catalysts: γCDCoBr$_2$ = complex (γ-cyclodextrin)CoBr$_2$; (DMC) dichloromethane; (EtAc) ethyl acetate.
[c] Percent substrate or product recovered by filtration, determined by ^{1}H NMR.
[d] Percent yield of oxidation product after isolation and purification.
[e] Specific optical rotation $[\alpha]_D^{21}$ [mm^{-1}x (g/100 mL)$^{-1}$] measured in acetone (C 2% at 21 °C λ = 589 nm).
[f] Without co-oxidant Fe(NO$_3$)$_3$·9H$_2$O.
[g] % catalyst (cat) with respect to the amount of substrate used in the experiment reported. This information is necessary for green calculations.
[h] Percent enantiomeric excess (% ee) [98].

solvents (dichloromethane and ethyl acetate) and/or different metallic centre Co or Ni has allowed us to analyze the greenness of our reaction conditions.

Compound **1** was oxidized with high yield and chemoselectivity using γCDCoBr$_{2(DCM)}$ or γCDCoBr$_{2(EtAc)}$. As can be observed in Table 4, we obtained 4-(methylsulfinyl) acetophenone **1a** with excellent yields when complexes of CoBr$_2$ were used, entries 6 and 7, whereas, CoBr$_2$ salt did not catalyze sulfoxidation reaction, entry 5. Entries 1–4 in Table 4 show than without the catalyst or without co-oxidant, there is no reaction. While all the reactions gave almost quantitative yield, the amount of isolated product was not the same since the work-up is in some cases more complicated than in others. No efforts were made to optimize the isolation procedures. Fe(NO$_3$)$_3$·9H$_2$O and CoBr$_2$ are soluble in the reaction system; this fact hinders the isolation from the reaction product with an important loss of the same.

On the other hand, the sulfoxidation catalyzed was very efficient over compound **2** and it was good over compound **3**, Tables 5 and 6. Under the same reaction conditions and during the same time, 5 h, sulfide oxidation was observed in the presence of co-oxidant alone. This is possible due to the greater availability of electronic density on sulfur atom in compounds **2**, **3**, and principally compound **4**, Table 7.

The results reported in Table 7 show the inhibition of sulfoxidation reaction in the presence of CoBr$_2$ salt and complexes γCDCoBr$_{2(DCM)}$ and γCDCoBr$_{2(EtAc)}$, entries 5, 6 and 7. This effect was observed also in compounds **3** when CoBr$_2$ was used as a catalyst, Table 6 entry 5.

In most cases and in agreement with TON − TOF values reported in this paper, the better catalyst was γCDCoBr$_{2(DCM)}$, entries 6 in Tables 4, 5 and 7. In no case was obtained a good enantiomeric excess.

On the other hand, γCDNiBr$_{2(EtAc)}$ was the best Nickel catalysts, entry 7 in Table 8, in agreement with TON − TOF values reported here. The γCDNiBr$_{2(DCM)}$ complex did not catalyze the sulfoxidation reaction. As in the case of Co Complexes, a good enantiomeric excess was not obtained.

3.5. Green evaluation

The results obtained in green evaluation are summarized in Table 9.

Table 5
Oxidation reaction of 4-(methylthio)benzaldehyde to 4-(methylsulfinyl) benzaldehyde with γCDCoBr$_2$ complexes or CoBr$_2$ as catalysts.[a]

Entry	Catalyst[b]	Substrate[c]	Yield[c] (%)[d] [polarimetry][e]	TON	TOF
1	– (29.3%oxid)[f]	80	20 (16.6)	(0.57)[g]	(0.11)[g]
2	CoBr$_2$[h]	100	–	–	–
3	γCDCoBr$_{2(DCM)}$[h]	100	–	–	–
4	γCDCoBr$_{2(EtAc)}$[h]	100	–	–	–
5	CoBr$_2$ (8.4%cat)[f]	9	91 (80.4)	9.59	1.92
6	γCDCoBr$_{2(DCM)}$ (7.8%cat)[f]	–	100 (92.7) [+0.57 (0.26)[i]]	11.86	2.37
7	γCDCoBr$_{2(EtAc)}$ (7.8%cat)[f]	1	99 (74.5) [+0.34 (0.18)[i]]	8.33	1.67

[a] Solvent acetonitrile, co-oxidant Fe(NO$_3$)$_3$·9 H$_2$O, ratio substrate: catalyst: co-oxidant 1.00: 0.10: 0.30 mol, at room temperature with stirring, under air, reaction time 5 h.
[b] Catalysts: γCDCoBr$_2$ = complex (γ-cyclodextrin)CoBr$_2$; (DMC) dichloromethane; (EtAc) ethyl acetate.
[c] Percent substrate or product recovered by filtration, determined by ^{1}H NMR.
[d] Percent yield of oxidation product after isolation and purification.
[e] Specific optical rotation $[\alpha]_D^{21}$ [mm^{-1}x (g/100 mL)$^{-1}$] measured in acetone (C 2% at 21 °C λ = 589 nm).
[f] % catalyst (cat) or co-oxidant (oxid) with respect to the amount of substrate used in the experiment reported. This information is necessary for green calculations.
[g] The value was calculated in relation to oxidant mol used.
[h] Without co-oxidant Fe(NO$_3$)$_3$·9 H$_2$O.
[i] Percent enantiomeric excess (% ee) [99].

Table 6
Oxidation reaction of 4-(methylthio)bromobenzene to 4-(methylsulfinyl) bromobenzene with γCDCoBr$_2$ complexes or CoBr$_2$ as catalysts.[a]

Entry	Catalyst[b]	Substrate[c]	Yield[c] (%)[d] [polarimetry][e]	TON	TOF
1	– (31.5%oxid)[f]	29	71 (38.3)	(1.22)[g]	(0.24)[g]
2	CoBr$_2$[h]	100	–	–	–
3	γCDCoBr$_{2(DCM)}$[h]	100	–	–	–
4	γCDCoBr$_{2(EtAc)}$[h]	100	–	–	–
5	CoBr$_2$ (10.0%cat)[f]	51	49 (29.9)	2.99	0.60
6	γCDCoBr$_{2(DCM)}$ (9.1%cat)[f]	5	95 (56.8) [-0.21(0.20; *S*)[i]]	6.23	1.25
7	γCDCoBr$_{2(EtAc)}$ (9.7%cat)[f]	–-	100 (61.2) [-0.27(0.26; *S*)[i]]	6.33	1.27

[a] Solvent acetonitrile, co-oxidant Fe(NO$_3$)$_3$·9 H$_2$O, ratio substrate: catalyst: co-oxidant 1.00: 0.10: 0.30 mol, at room temperature with stirring, under air, reaction time 5 h.
[b] Catalysts: γCDCoBr$_2$ = complex (γ-cyclodextrin)CoBr$_2$; (DMC) dichloromethane; (EtAc) ethyl acetate.
[c] Percent substrate or product recovered by filtration, determined by ^{1}H NMR.
[d] Percent yield of oxidation products after isolation and purification.
[e] Specific optical rotation $[\alpha]_D^{21}$ [mm^{-1}x(g/100 mL)$^{-1}$] measured in acetone (C 2% at 21 °C λ = 589 nm).
[f] % catalyst (cat) or co-oxidant (oxid) with respect to the amount of substrate used in the experiment reported. This information is necessary for green calculations.
[g] The value was calculated in relation to oxidant mol used.
[h] Without co-oxidant Fe(NO$_3$)$_3$·9 H$_2$O.
[i] Percent enantiomeric excess (% ee) [100].

The best result of each parameter to the different substrates is in bol.

AE data showed that sulfoxidation reaction studied here with molecular oxygen present in air as oxidant, 30% co-oxidant and catalyst, is a good reaction. For GSAI%, the complexes synthesized in ethyl acetate

Table 7
Oxidation reaction of 4-(methylthio)benzene to 4-(methylsulfinyl)benzene with γCDCoBr$_2$ complexes or CoBr$_2$ as catalysts.[a]

Entry	Catalyst[b]	Substrate[c]	Yield[c] (%)[d] [polarimetry][e]	TON	TOF
1	– (26.2%oxid)[f]	–	100 (62.7)	(5.92)[g]	(1.18)[g]
2	CoBr$_2$[h]	100	–	–	–
3	γCDCoBr$_{2(DCM)}$[h]	100	–	–	–
4	γCDCoBr$_{2(EtAc)}$[h]	100	–	–	–
5	CoBr$_2$ (10.1%cat)[f]	24	76 (45.6)	4.52	0.90
6	γCDCoBr$_{2(DCM)}$ (5.2%cat)[f]	7	93 (81.5) [-0.22 (0.15; *S*)[i]]	15.58	3.12
7	γCDCoBr$_{2(EtAc)}$ (5.1%cat)[f]	19	81 (68.4) [-0.14 (0.09; *S*)[i]]	13.50	2.70

[a] Solvent acetonitrile, co-oxidant Fe(NO$_3$)$_3$·9 H$_2$O, ratio substrate: catalyst: co-oxidant 1.00: 0.10: 0.30 mol, at room temperature with stirring, under air, reaction time 5 h.
[b] Catalysts: γCDCoBr$_2$ = complex (γ-cyclodextrin)CoBr$_2$; (DMC) dichloromethane; (EtAc) ethyl acetate.
[c] Percent substrate or product recovered by filtration, determined by ^{1}H NMR.
[d] Percent yield of oxidation product after isolation and purification.
[e] Specific optical rotation $[\alpha]_D^{21}$ [mm^{-1}*x* (g/100 mL)$^{-1}$] measured in acetone (C 2% at 21 °C λ = 589 nm).
[f] % catalyst (cat) or co-oxidant (oxid) with respect to the amount of substrate used in the experiment reported. This information is necessary for green calculations.
[g] The value was calculated in relation to oxidant mol used.
[h] Without co-oxidant Fe(NO$_3$)$_3$·9 H$_2$O.
[i] Percent enantiomeric excess (% ee) [101,102].

Table 8
Oxidation reaction of 4-(methylthio)benzaldehyde to 4-(methylsulfinyl) benzaldehyde with γCDNiBr$_2$ complexes or NiBr$_2$ as catalysts.[a]

Entry	Catalyst[b]	Substrate[c]	Yield[c] (%)[d] [polarimetry][e]	TON	TOF
1	– (28.8%oxid) [f]	80	20 (15.3)	(0.53)[g]	(0.11)[g]
2	NiBr$_2$[h]	100	–	–	–
3	γCDNiBr$_{2(DCM)}$ [h]	100	–	–	–
4	γCDNiBr$_{2(EtAc)}$ [h]	100	–	–	–
5	NiBr$_2$ (9.1%cat) [f]	13	87 (66.0)	7.28	1.46
6	γCDNiBr$_{2(DCM)}$ (9.9%cat) [f]	80	20 (14.6) [+0.15 (0.02)[i]]	1.48	0.30
7	γCDNiBr$_{2(EtAc)}$ (8.3%cat) [f]	4	96 (87.9) [+0.23 (0.08)[i]]	10.58	2.12

[a] Solvent acetonitrile, co-oxidant Fe(NO$_3$)$_3$·9 H$_2$O, ratio substrate: catalyst: co-oxidant 1.00: 0.10: 0.30 mol, at room temperature with stirring, under air, reaction time 5 h.
[b] Catalysts: γCDNiBr$_2$ = complex (γ-cyclodextrin)NiBr$_2$; (DMC) dichloromethane; (EtAc) ethyl acetate.
[c] Percent substrate or product recovered by filtration, determinate by ^{1}H NMR.
[d] Percent yield of oxidation product after isolation and purification.
[e] Specific optical rotation $[\alpha]_D^{21}$ [mm^{-1}*x* (g/100 mL)$^{-1}$] measured in acetone (C 2% at 21 °C λ = 589 nm).
[f] % catalyst (cat) or co-oxidant (oxid) with respect to the amount of substrate used in the experiment reported. This information is necessary for green calculations.
[g] The value was calculated in relation to oxidant mol used.
[h] Without co-oxidant Fe(NO$_3$)$_3$·9 H$_2$O.
[i] Percent enantiomeric excess (% ee) [99].

(a green solvent) showed the best performance. The other parameters are highly dependent on the yield and mass reactant used.

In general, the γCD complexes showed the best green results with all substrates.

Since enantiomeric excess was not obtained (sought based on what is reported in reference [23]) but it was obtained chemoselectivity, the changes that could be made to improve the values in the green parameters, using γCD complexes as catalysts, would be: to decrease the amount of solvent, co-oxidant and catalyst used in the reaction. This would improve MI and RME parameters. If both workup and purification are improved, EcoScale values will also increase.

3.6. General Comments

In our previous study with Cu(II) as metallic centre (see ref. [58]), we showed that the thermal stability of complexes depends markedly on the nature of both neutral and anionic ligands when all complexes were synthesized in the same solvent.

In this case, by comparing the values of T$_d$50%, it can be said that the presence of CoBr$_2$ or NiBr$_2$ modifies the stability of macrocycle; however, the effect over the complexes of solvent used in the synthetic process is more important.

T$_d$50% is frequently used to compare the thermal stability of solids. In our complexes, these values are useful since important differences between T$_d$50% were found for the complexes between them and the γCD.

The decomposition starts at a lower temperature in the complexes, this is observed in the analyses by DTGA curves. Between them, fragments of complexes synthesized in DCM are slowly liberated probably due to remain coordinated with the metal centre. So, the carbohydrate is thermally destabilized by the presence of a metallic salt.

Besides, in the percentage of remaining mass is evidenced the effect of salt coordination and the synthetic solvent since it is high in γCDNiBr$_2$(DCM) decomposition (30.94%) or low in γCDNiBr$_2$(EtAc) (6.49%).

All the results indicate that the structure of complexes is determined not only by the metal coordination with γ-cyclodextrin but also by the solvent used in the synthesis itself. The difference in color, ΔE, (> 5) shows that complexes synthesized in DCM and EtAc solvents are different.

The different thermal stability helps to understand the behaviour of complexes as catalysts, where γCDNiBr$_2$(DCM) is the least active.

The reactions reported here, from the green chemistry point of view, follow several of its principles and have very good green metrics. It is also important to note that the green evaluation has been performed from the synthesis of the catalysts used.

4. Conclusion

We were determined that CoBr$_2$ and NiBr$_2$ form stable complexes with γCD in dichloromethane or ethyl acetate as synthesis solvents. The synthetic methodology is simple and yield complexes with 1:1 (γCD: CoBr$_2$ or NiBr$_2$) stoichiometry. These complexes also contains water molecules. After comparison of their TGA analysis, UV–vis and IR spectra, we could observed and determined that the structure of the complexes obtained in several repetitive syntheses was reproductible.

We could determine the stoichiometry and the predominant interactions and some structural information of the Co^{2+} or Ni^{2+} complexes in different solvents. For this, the integration of analytical data obtained by several techniques (EA, TGA, UV–vis and FT-IR) and the standardized method for the study of metal complexes was used [60]. Through reflectance measurements, complexes showed have octahedral coordination geometry, but with varying degrees of distortion. CIELab colorimetric data showed the differences between the complexes synthesized. This methodology is easily applied and is very useful for the rapid characterization of complexes in their second synthesis. It should be noted that, despite the great utility of the last two techniques discussed, we have found little literature on its use in the characterization of catalysts.

We report herein a green and efficient method for the selective oxidation of sulfides to sulfoxides under very mild heterogeneous

Table 9
Green parameters of sulfoxidation reactions.

Entry	Catalyst	GSAI%	Yield%[a] (%oxid)[b]	EcoScale	MI	RME	AE
Sulfoxidation of 4-(methylthio)acetophenone to 4-(methylsulfinyl)acetophenone.							
1	γCDCoBr$_{2(DCM)}$	77.5	76.7 (24.3%oxid)	69.4	**51.0**	**45.9**	91.9
2	γCDCoBr$_{2(EtAc)}$	**86.0**	**79.1** (28.8%oxid)	**70.6**	58.4	43.8	91.9
Sulfoxidation of 4-(methylthio)benzaldehyde to 4-(methylsulfinyl)benzaldehyde.							
3	–	65.0	16.6 (29.3%oxid)	39.3	101.6	9.8	91.3
4	$CoBr_2$	62.50	80.4 (26.2%oxid)	71.2	18.9	49.8	91.3
5	γCDCoBr$_{2(DCM)}$	77.5	**92.7** (26.6%oxid)	**77.4**	**15.5**	**57.4**	91.3
6	γCDCoBr$_{2(EtAc)}$	**86.0**	74.5 (30.1%oxid)	68.3	21.7	43.6	91.3
Sulfoxidation of 4-(methylthio)bromobenzene to 4-(methylsulfinyl)bromobenzene.							
7	–	65.0	38.3 (31.5%oxid)	50.2	57.3	15.5	93.2
8	$CoBr_2$	62.5	29.9 (33.7%oxid)	46.0	73.4	11.8	93.2
9	γCDCoBr$_{2(DCM)}$	77.5	56.8 (28.8%oxid)	59.4	35.4	23.9	93.2
10	γCDCoBr$_{2(EtAc)}$	**86.0**	**61.2** (29.4%oxid)	**61.6**	**34.6**	**25.5**	93.2
Sulfoxidation of 4-(methylthio)benzene to 4-(methylsulfinyl)benzene.							
11	–	65.0	62.7 (26.2%oxid)	62.4	28.7	36.1	89.8
12	$CoBr_2$	62.5	45.6 (31.8%oxid)	53.8	47.1	23.8	89.8
13	γCDCoBr$_{2(DCM)}$	77.5	**81.5** (16.2%oxid)	**71.8**	**14.2**	**57.8**	89.8
14	γCDCoBr$_{2(EtAc)}$	**86.0**	68.4 (17.0%oxid)	65.2	16.5	47.7	89.8
Sulfoxidation of 4-(methylthio)benzaldehyde to 4-(methylsulfinyl)benzaldehyde.							
15	–	65.0	15.3 (28.8%oxid)	38.7	108.8	9.1	91.3
16	$NiBr_2$	62.5	66.0 (28.5%oxid)	64.0	24.8	39.4	91.3
17	γCDNiBr$_{2(DCM)}$	77.5	14.6 (33.4%oxid)	38.3	121.5	8.1	91.3
18	γCDNiBr$_{2(EtAc)}$	**86.0**	**87.9** (26.0%oxid)	**75.0**	**17.1**	**54.7**	91.3

[a] Percent yield of oxidation product after isolation and purification.
[b] % co-oxidant (oxid) with respect to the amount of substrate used in the experiment reported. This information is necessary for green calculations.

conditions with high yields and excellent chemoselectivity. This sulfoxidation method could have scope or be applicable in molecules with more complex structures containing aryl sulfides with electron-withdrawing groups. A good comparison of complexes of γCD was also made as catalysts.

The type of green evaluation carried out in this study allows us to project changes to improve the work methodology. It allows evaluating, for example, if it is more beneficial to change to a greener solvent that produces less effective catalysts or to use a less environmentally friendly solvent that can be recycled in the synthesis of the same complex. Undoubtedly, a holistic and global analysis allows to better understanding of the chemical reactions and processes involved.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.mcat.2018.05.004.

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