

## PREPARATION AND IMMOBILIZATION OF diNOsarcobalt(III) COMPLEX IN ZEOLITE Y FOR THE CATALYZED PRODUCTION OF HYDROGEN PEROXIDE

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A complex cation, diNOsarcobalt(III),  $[\text{Co}(\text{diNOsar})]^{3+}$ , (diNOsar = 1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo-[6.6.6]heicosane), was synthesized and immobilized in the cavities of a Y zeolite by the reaction of precursor species in the pores of the zeolite. The encapsulated material was compared to the compound diNOsarcobalt(III) chloride,  $[\text{Co}(\text{diNOsar})]\text{Cl}_3$ . Both diNOsarcobalt(III) chloride and the zeolite-encapsulated complex,  $[\text{Co}(\text{diNOsar})]^{3+}/\text{zeolite}$ , were obtained in high yield and characterized by ultraviolet-visible and infrared spectroscopy. X-ray diffraction demonstrated the incorporation of the complex cation into the pores of the zeolite. The catalytic production of hydrogen peroxide from oxygenated water confirmed the successful synthesis of the complex diNOsarcobalt(III) immobilized in the zeolite.

Keywords: diNOsarcobalt(III) chloride; hydrogen peroxide; Y zeolite.

### INTRODUCTION

Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is considered an inorganic compound of elevated consumption in the chemical industry; this compound is used as a raw material in numerous production processes, and as a powerful oxidizing agent in several reactions of environmental impact.<sup>1-3</sup> Several studies demonstrate the importance of understanding the reactions and applications of this compound.<sup>4-7</sup> Among different conventional applications, hydrogen peroxide is used in place of bleach in textile factories and in paper production, as a disinfectant for the cleaning of implements (bottles, cans and machines) that are used in the food industry, and in the production of a broad variety of organic and inorganic chemicals. In organic synthesis, hydrogen peroxide is used to prepare organic peroxides and perform polymerization reactions. Furthermore, hydrogen peroxide is employed to clean metals and electronic devices,<sup>8</sup> to design new fuel cells,<sup>7</sup> and to purify wastewater via Fenton and Fenton-type processes.<sup>1,3</sup>

The earliest method for hydrogen peroxide production was proposed by L. J. Thenard in 1818, based on the reaction of barium peroxide with nitric acid; slightly modified, this method became an industrial procedure sixty years later and persisted until the middle of the twentieth century. Successive procedures were later developed (e.g., electrolytic methods or those employing oxidation of 2-propanol), but most of the industrial processes in use today produce  $\text{H}_2\text{O}_2$  via the anthraquinone/anthrahydroquinone system.<sup>1</sup> This procedure, known as “the anthraquinone process”, is chemically based on the reaction described in Figure 1, and provides a higher yield of hydrogen peroxide at lower costs than the previously mentioned procedures. However, the anthraquinone process has a number of known difficulties that have focused attention toward its optimization, and motivated the development of new synthetic approaches.<sup>1</sup> For example, the anthraquinone method produces organic byproducts generated from secondary transformations of anthraquinone; thus it requires additional separation procedures. Furthermore, anthrahydroquinone requires aromatic solvents, while anthraquinone requires polar solvents such as alcohols and esters. This situation leads to the use of frequently expensive and complex mixtures of solvents, and

the recovery operations can also be complicated. The hydrogenation step of the anthraquinone process furthermore uses Pd catalysts (Figure 1), which are expensive and can be deactivated by interaction with organic byproducts formed in the reaction.<sup>1</sup> Organic byproducts of  $\text{H}_2\text{O}_2$  synthesis can also have a detrimental effect on the stability of hydrogen peroxide solutions. Raney nickel catalysts, which are sometimes used in place of palladium catalysts, require more stringent safety procedures for handling because of their extremely pyrophoric behavior.<sup>1</sup>

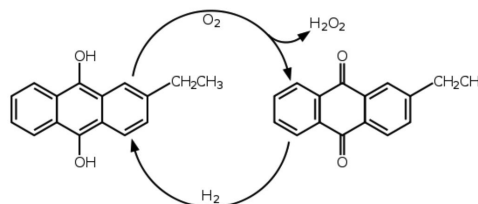
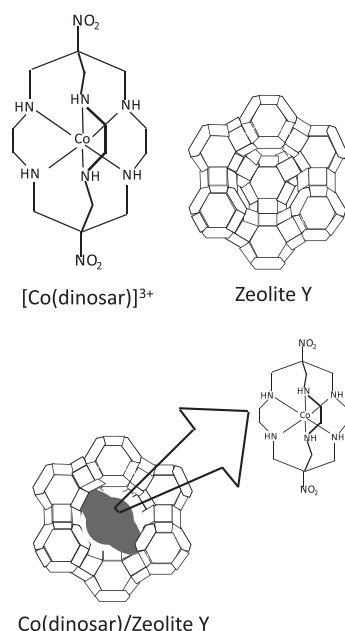


Figure 1. Schematic representation of the fundamental reactions involved in the anthraquinone method for producing hydrogen peroxide

Sargeson *et al.*<sup>9</sup> proposed the synthesis of hydrogen peroxide from oxygen dissolved in water, using as a homogeneous catalyst a cobalt-containing coordination compound known as an “encapsulated complex” or “cage compound”. The water-soluble cobalt cage compound (1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo-[6.6.6]heicosan) cobalt(III) chloride, abbreviated as diNOsarcobalt(III) chloride or  $[\text{Co}(\text{diNOsar})]\text{Cl}_3$ , (Figure 2) has excellent catalytic properties for this reaction, and its synthesis has been widely published in the literature.<sup>10,11</sup> However, the use of this catalyst in homogeneous medium requires additional complex separation procedures for isolation before a possible distillation for concentrating the hydrogen peroxide solutions. The present work investigates the synthesis of the complex cation, known as diNOsarcobalt(III) ( $[\text{Co}(\text{diNOsar})]^{3+}$ ), inside a water-insoluble porous solid that allows separation from the reaction medium (Figure 2).

Zeolites are insoluble solids that can exhibit the required characteristics and appropriate pore size to contain the  $[\text{Co}(\text{diNOsar})]^{3+}$  cation, without releasing the cation after synthesis. These solids are aluminosilicates (tectosilicates), whose structure comprises tridimensional

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**Figure 2.** Structures of the complex diNOsarcobalt(III) ( $[Co(diNOsar)]^{3+}$ ), (1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo-(6.6.6)icosane)cobalt(III), Zeolite Y, and the complex cation inside the zeolite ("ship in a bottle"-type immobilization)

frameworks of  $SiO_4$  and  $AlO_4$  groups linked through shared oxygen atoms. This structure has channels and cages of molecular dimensions that form a microporous network.<sup>12</sup> Zeolite Y exhibits a microporous structure with "supercages" that are large enough to accommodate spheres with 13 Å diameter; the supercages are connected by small cages of 8 Å diameter.<sup>12,13</sup> The present work is aimed at the synthesis of the complex cation  $[Co(diNOsar)]^{3+}$  "in situ" (inside the zeolite cages) to make a "ship in a bottle"-type immobilized system (Figure 2).<sup>14</sup> This study advances the development of heterogeneous catalysts for hydrogen peroxide production. The sizes of the molecules involved in the synthesis are known to be 8 Å for diNOsarcobalt(III) chloride and 4.8 Å for the precursor, tris(ethylenediamine)cobalt(III) chloride.<sup>15</sup>

## EXPERIMENT

### Synthesis of free diNOsarcobalt(III) chloride

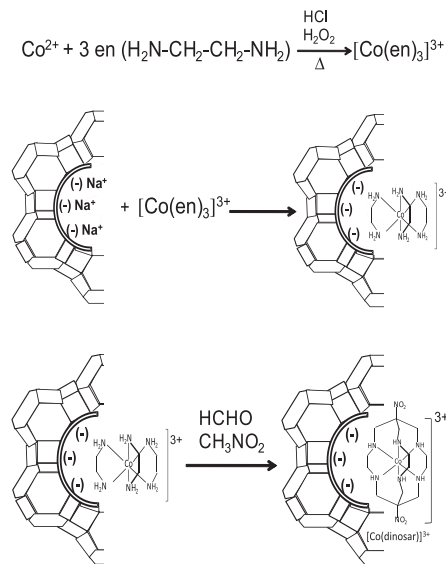
The precursor tris(ethylenediamine)cobalt(III) chloride,  $[Co(en)_3]Cl_3$ , was first prepared. The synthesis of this compound is widely recognized in inorganic chemistry.<sup>16,17</sup> A 30 g sample of  $CoCl_2 \cdot 6H_2O$  (Merck, analytical grade) was dissolved in 87.5 mL of distilled water (solution A). Meanwhile, a solution B was prepared by adding 22.5 mL of concentrated HCl, under continuous stirring and cooling in an ice bath, to a mixture of 22.5 mL ethylenediamine (Merck) in 62.5 mL distilled water. The solution A was slowly added to the solution B and then mixed with 25.0 mL of 30% hydrogen peroxide (Panreac). After 10 minutes under continuous stirring, the final mixture was heated to gentle boiling. After the volume had reduced to 150 mL, an equal volume of concentrated hydrochloric acid was added, followed by addition of 300 mL ethanol. The mixture was cooled in an ice bath, and the solid was vacuum-filtered. The resulting solid, tris(ethylenediamine)cobalt(III) chloride, was washed with two portions of ethanol and two portions of diethyl ether.

The complex  $[Co(diNOsar)]Cl_3$  was synthesized according to the literature.<sup>9-11</sup> All of precursor  $[Co(en)_3]Cl_3$  (12.5 g) was dissolved in distilled water (125 mL) with 6.0 g of  $Na_2CO_3$ . To this mixture, 90

mL of a 40% aqueous formaldehyde solution (Merck) and 14.7 mL of nitromethane (Merck) were added. This mixture was incubated at 40 °C for 90 minutes, and the resultant precipitate was vacuum-filtered. A hot solution of 3 M HCl (60 mL) was added to dissolve and re-crystallize the precipitate. The solution was cooled in ice water, and 100 mL of ethanol was added. The  $[Co(diNOsar)]Cl_3$  was obtained as a re-crystallized solid and isolated by vacuum filtration.

### Synthesis of immobilized $[Co(diNOsar)]^{3+}$ cation

This synthesis was performed by initial incorporation of the precursor cation  $[Co(en)_3]^{3+}$  in the cavities of Zeolite Y, and the subsequent synthesis of the complex diNOsarcobalt(III) (Figure 3). The incorporation of the precursor inside the zeolite cages is based on the cationic exchange capacity of this zeolite (78 meq/100 g). According to this value, 2 g of zeolite should be able to incorporate 0.12 g of precursor. The zeolite (2 g) was exchanged with a precursor solution (25 mL, containing  $5 \times 10^{-4}$  moles of  $[Co(en)_3]^{3+}$ ) for 24 hours under continuous stirring. After this time, the solid was removed by centrifugation and washed with deionized water. To ensure higher incorporation of the cation, the resultant solid was subjected to a second cationic exchange. The solid was washed with deionized water until all of the chloride was removed. Next, the  $[Co(diNOsar)]^{3+}$  was synthesized in the zeolite according to the procedure described above. After each reactant addition, the system was left for 5 hours under continuous stirring to allow inclusion of the chemical species in the zeolite pores. Finally, the solid was separated by centrifugation and washed with deionized water until all of the chloride was removed. Washing the solid removes chemical species retained outside the zeolite cages.



**Figure 3.** Scheme of reactions to synthesize the complex diNOsarcobalt(III) ( $[Co(diNOsar)]^{3+}$ ) inside the pores of Zeolite Y by a "ship in a bottle"-type immobilization

### Analytical techniques

Cobalt was quantified, and the ultraviolet-visible (UV-Vis) absorption profiles were obtained, using a VARIAN Cary 50 (UV-Vis) spectrometer. Cobalt determination was performed at 520 nm after dissolution of the coordination compound ( $[Co(diNOsar)]Cl_3$ ) in concentrated sulfuric acid. For the immobilized coordination complex, the solid was previously treated with hydrofluoric acid to dissolve the zeolite.

IR spectroscopy was performed using a Perkin Elmer (FT-IR) Paragon 500. For each analysis, the sample was mixed with KBr (2 mg of sample in 200 mg of KBr) and was compressed to form a transparent tablet. X-ray powder diffraction was carried out on an X-Pert Pro MPD PANalytical diffractometer (Cu K $\alpha$  = 1.54060 Å) with 2 $\theta$  geometry and Bragg-Brentano configuration at room temperature using a step size of 0.01° and a step time of 10 s. The apparent density of the solids was measured using a 5 mL pycnometer (DIN) with ether.

### Hydrogen peroxide formation

The formation of H<sub>2</sub>O<sub>2</sub> from oxygen dissolved in water was monitored according to the procedure described by Sargeson *et al.*<sup>9</sup> with slight modifications. Solid catalyst (0.1 g) was added to 50 mL of distilled/deionized water (resistivity: 14.2 M $\Omega$ .cm) at room temperature (20 °C, controlled with a thermostat) with constant stirring. Sodium borohydride, NaBH<sub>4</sub>, (0.3 g, Sigma-Aldrich, 98%) was added to reduce Co(III) to Co(II) in the complex cation diNOsarcobalt(III). Next, the solution was acidified with 0.5 mL of 1 M HCl. Finally, O<sub>2</sub> (2 mL/min) was bubbled into the aqueous suspension for 2 hours. It is worthwhile to mention that the structure of the complex is maintained despite the change in the oxidation number of the metal ion from Co(III) to Co(II), so that diNOsarcobalt(III) is a stable precursor and the active species contains Co(II). The catalytic cycle comprises the oxidizing of a coordination complex that contains a metal ion capable of existing in at least two oxidation states, said coordination complex being sufficiently stable for the metal ion to be oxidized and reduced without decomposition of the complex; the cycle begins with said metal ion in its lower oxidation state.<sup>9</sup>

Hydrogen peroxide produced during the reaction was quantified by the production of oxygen from the catalyzed decomposition of hydrogen peroxide with potassium iodide (KI). The reaction suspension (water and catalyst) was filtered, and the resulting solution was placed in a sealed and temperature-controlled (20 °C) container of 100 mL volume. KI (0.1 g) was then added, and the oxygen produced over several minutes was quantified using a differential pressure sensor (MPX 2010), assuming that an increase of pressure in this system arises entirely from the oxygen produced by the catalyzed decomposition of H<sub>2</sub>O<sub>2</sub>. This sensor was connected to a multimeter (UT60E RS232C) and a computer (software UT60E Interface Program\_ver 2.02).<sup>18</sup>

## RESULTS AND DISCUSSION

Figure 1S shows the visual characteristics of diNOsarcobalt(III) chloride (Figure 1S-b) and tris(ethylenediamine)cobalt(III) chloride (Figure 1S-a). The characteristic color of these compounds has been reported in the literature.<sup>9-11</sup> Figures 1S-c and 1S-d show that the initial color of the zeolite is white, and its change to yellow results from the incorporation of the complex cation [Co(diNOsar)]<sup>3+</sup>.

Two characteristic signals, corresponding to the coordination of cobalt ions with ethylenediamine ligands in the complex cation [Co(diNOsar)]<sup>3+</sup>, are visible in the UV-Vis spectra of diNOsar in the free coordination compound, diNOsarcobalt(III) chloride, and the complex/zeolite system in aqueous solution (Figure 2S). Absorption bands measuring approximately 475 nm and 340 nm correspond to Co<sup>3+</sup> coordinated with six atoms of nitrogen, which belong to the three ethylenediamine ligands in the structure of the complex cation [Co(diNOsar)]<sup>3+</sup>.<sup>9-11,19</sup>

The percentage of cobalt was determined to be 10% for both the free diNOsarcobalt(III) chloride and the fraction of immobilized complex. This is in good agreement with the cobalt percentage experimentally determined for diNOsarcobalt(III) chloride in previous works, which is 10.6%.<sup>9,10</sup>

The apparent density of the [Co(diNOsar)]<sup>3+</sup>-containing zeolite is higher than that of free diNOsarcobalt(III) chloride and Zeolite Y considered separately (Table 1). Such an increase can be attributed to the incorporation of the cation [Co(diNOsar)]<sup>3+</sup> into the zeolite pores. Along with the UV-Vis spectra, these results provide the first indication of the successful incorporation of the complex cation into the zeolite.

**Table 1.** Apparent density of the studied solids

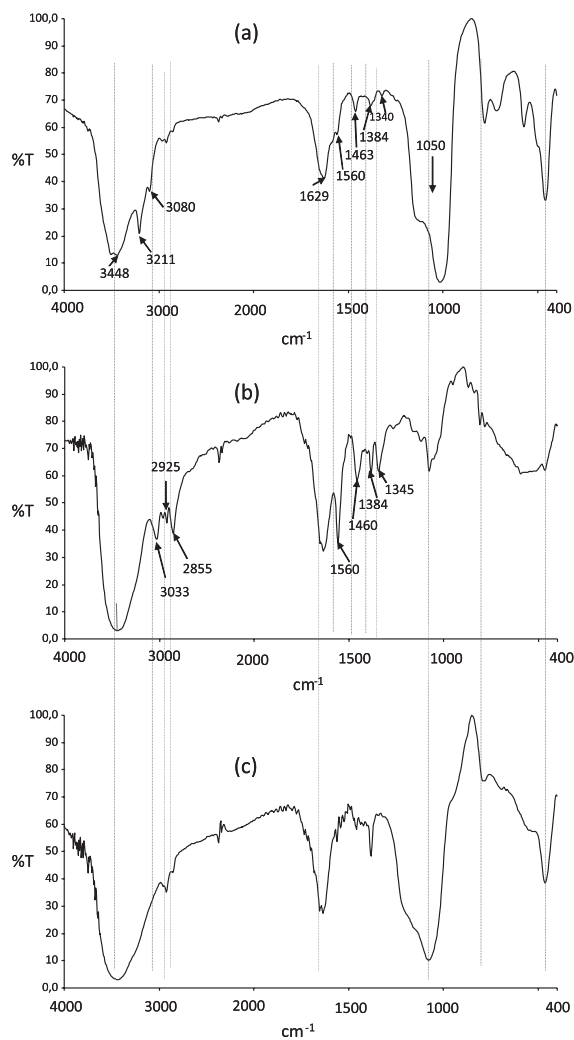
Material	Density (g/cm <sup>3</sup> )
[Co(en) <sub>3</sub> ]Cl <sub>3</sub>	1.5
[Co(diNOsar)]Cl <sub>3</sub>	1.7*
Zeolite Y	1.4
[Co(diNOsar)] <sup>3+</sup> /zeolita Y	2.1

\*Density value reported by Geue *et al.*<sup>10</sup> is 1.6 g/cm<sup>3</sup>.

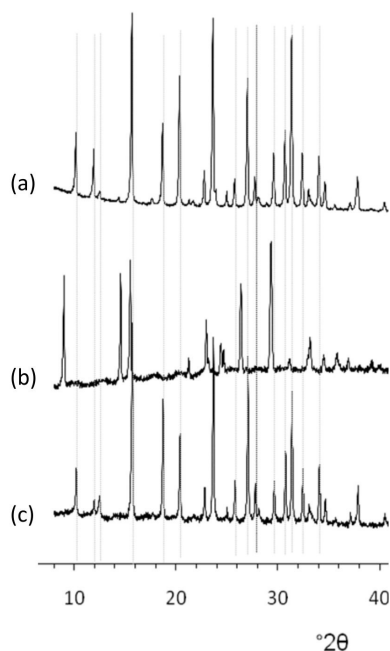
IR spectroscopy (Figure 4) shows the characteristic signals for the prepared materials and for the zeolite used as support. Figure 4c shows the spectrum of Zeolite Y. A band at approximately 1050 cm<sup>-1</sup> results from the stretching vibrations of Si–O bonds in this aluminosilicate, and the bands that appear between 400 and 900 cm<sup>-1</sup> result from several vibrations of Si–O and Al–O bonds in the SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra.<sup>20</sup> Signals at approximately 3448 and 1629 cm<sup>-1</sup> in all of the IR spectra are attributed to the stretching and bending modes of –OH groups in adsorbed water.<sup>21,22</sup> DiNOsarcobalt(III) chloride exhibits a stretching band corresponding to N–H bonds, at 3033 cm<sup>-1</sup>,<sup>19</sup> as well as bands attributed to symmetrical and asymmetrical stretching vibrations of methylene groups (–CH<sub>2</sub>–) at 2855 and 2925 cm<sup>-1</sup>,<sup>22,23</sup> respectively (Figure 4b). IR signals at 1384 and 1460 cm<sup>-1</sup> correspond to the bending vibrations of methylene groups.<sup>21,22</sup> Peaks at 1345 and 1560 cm<sup>-1</sup> are attributed to symmetrical and asymmetrical stretching vibrations, respectively, of nitro (–NO<sub>2</sub>) groups in the [Co(diNOsar)]<sup>3+</sup> complex,<sup>10,15,21</sup> confirming the successful synthesis of this compound.<sup>10,11,15</sup>

Figure 4a shows the IR spectrum of the cation [Co(diNOsar)]<sup>3+</sup> immobilized in Zeolite Y. Characteristic bands of both the diNOsarcobalt(III) complex cation and the microporous solid (zeolite) were observed, showing the joint existence of these structures in the as-prepared material. The signals at 1340 and 1560 cm<sup>-1</sup> correspond to –NO<sub>2</sub> groups of the coordination complex. These results, along with those in Figures 4b and 4c, confirm the successful incorporation of the complex cation into the zeolite. The greater intensity of IR vibrations for the zeolite, compared to those of the complex cation alone, arises from the low quantity of the coordination complex in the material.

Figure 5 shows the crystalline profiles of diNOsarcobalt(III) chloride, the microporous support, and the zeolite containing the immobilized complex. X-ray diffraction (XRD) peaks of the immobilized complex within the zeolite (Figure 5c) are the same as those previously verified for Zeolite Y (Figure 5a)<sup>13</sup> indicating that the aluminosilicate structure was maintained after the preparative procedures and washing steps. Although diNOsarcobalt(III) chloride displays a crystal structure on its own (Figure 5b), [Co(diNOsar)]<sup>3+</sup> does not exhibit the characteristic XRD signals when incorporated into Zeolite Y, probably because the small size of the zeolite pores limits the assembly of [Co(diNOsar)]<sup>3+</sup> into crystal structures with long-range order. Considering that several washes were performed during purification of this mixed solid, and that the characteristic IR signals of diNOsarcobalt(III) complex were observed, the absence of XRD peaks for this complex confirms the successful synthesis of [Co(diNOsar)]<sup>3+</sup> into the pores of the zeolite to yield a “ship in a bottle” system.



**Figure 4.** IR spectra of the studied solids. **a)** Complex cation  $[\text{Co}(\text{diNOsar})]^{3+}$  immobilized in Zeolite Y. **b)** Free diNOsarcobalt(III) chloride. **c)** Zeolite Y



**Figure 5.** X-ray powder diffraction patterns of the obtained materials and the microporous solid used as support. **a)** Zeolite Y. **b)** DiNOsarcobalt(III) chloride. **c)** Zeolite Y containing the immobilized complex cation  $[\text{Co}(\text{diNOsar})]^{3+}$

Leaching of the complex cation from the zeolite was investigated by stirring this material in abundant 2 M hydrochloric acid solution for 24 hours at room temperature. The results showed no leaching for the  $[\text{Co}(\text{diNOsar})]^{3+}$  cation and for the cobalt soluble species, which further verifies the effective inclusion of complex cation in the zeolite.

Catalytic tests showed successful production of hydrogen peroxide from oxygen-saturated aqueous solution using either diNOsarcobalt(III) chloride or the complex  $[\text{Co}(\text{diNOsar})]^{3+}$  supported in the zeolite as catalysts. Figure 3Sa displays the assessment of  $\text{H}_2\text{O}_2$  produced through a catalytic experiment using the complex diNOsarcobalt(III) immobilized in Zeolite Y; the heterogeneous system contains 0.02 millimoles of complex cation. Stoichiometric correlation indicated a maximum  $\text{H}_2\text{O}_2$  concentration of 0.15 mol/L. However, nearly twofold higher levels of  $\text{H}_2\text{O}_2$  were produced using free diNOsarcobalt(III) chloride, a homogeneous system with 0.2 millimoles of complex cation, versus the heterogeneous system (Figure 3Sb), probably because the quantity of coordination cation available in the zeolite/ $[\text{Co}(\text{diNOsar})]^{3+}$  mixed material is only 10% of that available in the homogeneous catalyst. The bare zeolite exhibited no catalytic activity towards the production of hydrogen peroxide. The catalyzed production of hydrogen peroxide confirms the successful synthesis of both diNOsarcobalt(III) chloride and the complex  $[\text{Co}(\text{diNOsar})]^{3+}$  immobilized in the Y zeolite.

## CONCLUSION

UV-Vis and IR spectroscopy demonstrated the synthesis of both diNOsarcobalt(III) chloride and the complex cation  $[\text{Co}(\text{diNOsar})]^{3+}$  incorporated into Zeolite Y. X-ray powder diffraction revealed inclusion of the complex cation into the zeolite pores, and demonstrated the stability of this microporous support (Zeolite Y) under the chemical and physical treatments performed during the synthesis. Additionally, the catalytic activity of the as-prepared materials towards the production of hydrogen peroxide from dissolved oxygen in water verifies the successful synthesis of the diNOsarcobalt(III) complex, both free as chloride and immobilized in the porous solid. These results advance the design of efficient heterogeneous catalytic systems for the clean production of hydrogen peroxide.

## SUPPLEMENTARY MATERIAL

Available at <http://quimicanova.sbq.org.br>, in PDF file, with free access. Photographs of the synthesized solids (Figure 1S), UV-Vis spectra of the complex cation  $[\text{Co}(\text{diNOsar})]^{3+}$  in aqueous solution compared to the UV-Vis spectrum of tris(ethylenediamine) cobalt(III) chloride (Figure 2S), and the assessment of hydrogen peroxide production catalyzed by the complex diNOsarcobalt(III) ( $[\text{Co}(\text{diNOsar})]^{3+}$ ) immobilized in Zeolite Y versus the free diNOsarcobalt(III) chloride (Figure 3S).

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