

Zn-METALLOPORPHYRINS CONTAINING PYRIDYL GROUPS AND THEIR COMPARATIVE CAPACITY TO COORDINATE HEXACHLOROPLATINIC ACID

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Abstract

Two Zn-metalloporphyrins, both containing at least one-pyridyl group, were studied regarding their capacity to complex hexachloroplatinic acid comprised in leaching solutions and resulted after hydrometallurgical processes on spent automotive catalysts. The number of pyridyl groups and the steric and electronic influences from surrounding groups determine a different type of coordination with the hexachloroplatinic acid from solution, and surprisingly, although containing only one group of basic pyridyl, the unsymmetrical Zn(II)-5-pyridyl-10,15,20-tris-(3,4-di-methoxy-phenyl)-porphyrin had a removal capacity of 98% higher than that of Zn(II)-*meso*-tetrakis-pyridylporphyrin, substituted with four pyridyl groups, but with only a removal capacity of 84 % .

Introduction

The platinum is an expensive and rare element, so that its recovery must be appropriately considered. Several compounds are able to generate complexes with hexachloroplatinic acid. Among them, metalloporphyrins, due to their capacity to coordinate ligands at the metal centers [1], have to be analyzed. In this study, Zn(II)-tetrakis-pyridylporphyrin and Zn(II)-5-pyridyl-10,15,20-tris-(3,4-di-methoxy-phenyl)-porphyrin were investigated for their capacity to form complexes with hexachloroplatinic acid.

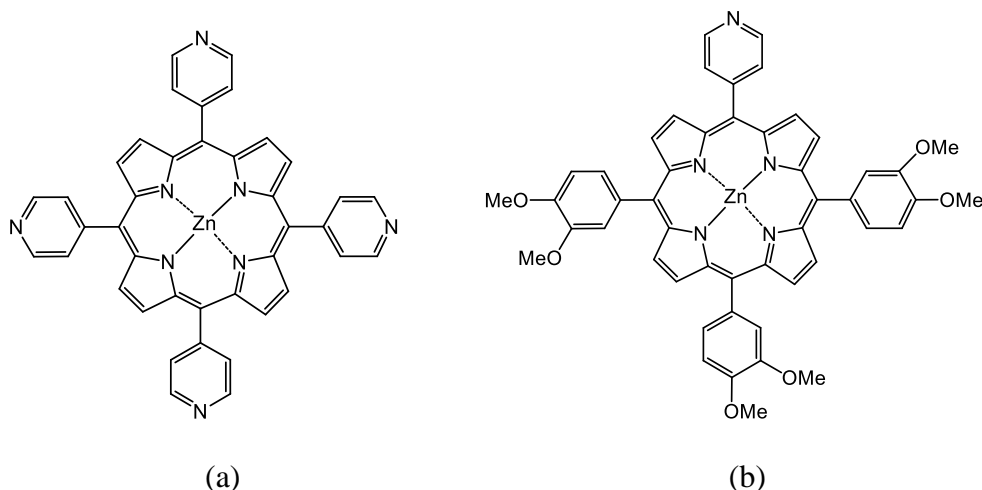


Figure 1. Structure of the investigated compounds: Zn(II)-tetrakis-pyridylporphyrin (a); Zn(II)-5-pyridyl-10,15,20-tris-(3,4-di-methoxy-phenyl)-porphyrin (b)

Materials and methods

Reagents. The Zn(II) metalloporphyrins were obtained in our laboratory and reported previously [2, 3]. N,N-Dimethylformamide was aquired from Merck (Darmstadt, Germany), hexachloroplatinic acid was obtained from Sigma-Aldrich (St. Louis, USA).

Methods. In the first case of Zn(II)-tetrakis-pyridylporphyrin, the experiments were performed by taking 5 mL porphyrin in DMF ($c = 4.49 \times 10^{-6}$ M) and adding at each step 0.05 mL hexachloroplatinic acid solution in water of 1.03×10^{-3} M concentration. Each mixture was stirred for 2 minutes and after, the UV-vis spectrum was recorded.

In the second case regarding Zn(II)-5-pyridyl-10,15,20-tris-(3,4-di-methoxy-phenyl)-porphyrin the method was similar but the porphyrin concentration was 1.192×10^{-5} M in DMF. The hexachloroplatinic acid concentration was the same. The amounts of hexachloroplatinic acid that were added differed from one sample to another.

Apparatus. For recording UV-visible spectra, standard 1 cm pass quartz cells were used on a JASCO UV- V-650 spectrometer (Japan).

Results and Discussions

The superposed spectra for the successive adding of chloroplatinic acid to the solution of the Zn(II)-tetrakis-pyridylporphyrin (Zn-TPyP) are presented in Figure 2, and to the Zn(II)-5-pyridyl-10,15,20-tris-(3,4-di-methoxy-phenyl)-porphyrin (Zn-Py-3,4diMeOPP), respectively in Figure 3.

As can easily be seen, the UV-vis spectrum of Zn-TPyP (figured in black) has the main characteristics of a metalloporphyrin, the Soret band around 425 nm and only two Q bands (due to higher symmetry), located at 575 nm and 625 nm respectively. In the course of increasing the hexachloroplatinic acid concentration, some changes are occurring, as follows: all the absorption bands are blue shifted with around 15 nm, and all the bands are suffering a hyperchromic effect.

Many isosbestic points are accompanying these changes (at 412 nm, 545 nm, 605 and 615 nm), proving that a lot of equilibrium processes are taking place and the complex formation can be explained on the pyridyl groups protonation, that are alternatively forming and breaking.

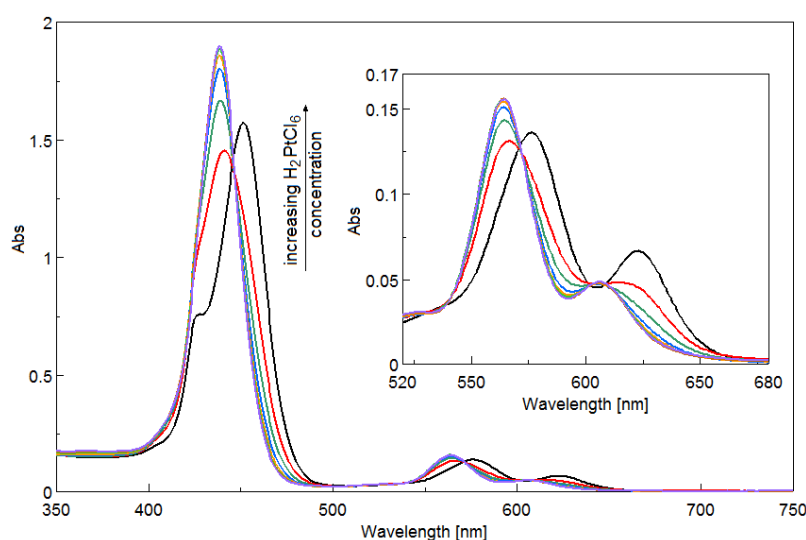


Figure 2. Overlapped UV-vis spectra after adding H_2PtCl_6 solution in water to Zn-TPyP solution in DMF. Details of the Q bands

A completely different phenomenon is produced regarding Zn-Py-3,4diMeOPP. In this case by increasing the hexachloroplatinic acid concentration the Soret band decreases in intensity and also the two Q bands. Only three isosbestic points are appearing at 405 nm and around 440 nm, on both branches of Soret and on the Q band at 640 nm (Figure 3).

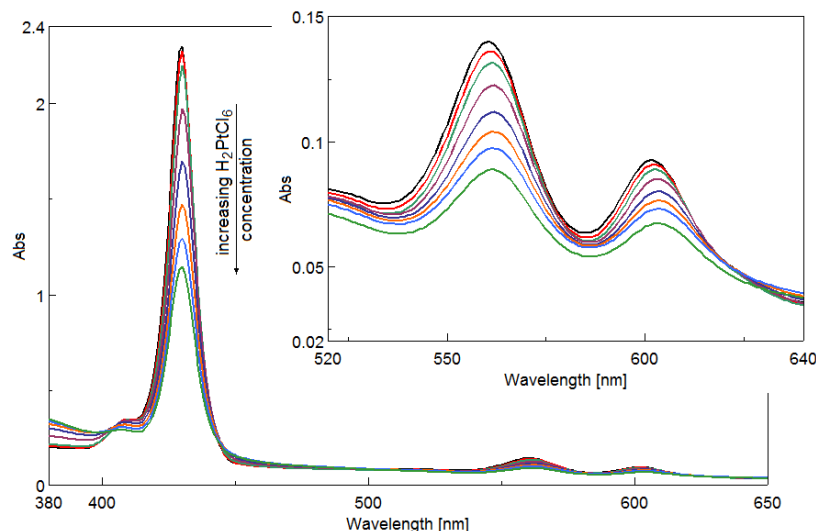


Figure 3. Overlapped UV-vis spectra after adding H_2PtCl_6 solution to a solution of Zn-Py-3,4diMeOPP in DMF. Detail of the isosbestic point at 640 nm

The dependences (polynomial and linear) between the intensity of absorption read at the Soret wavelength maxima and the H_2PtCl_6 concentration for the two Zn-metalloporphyrins porphyrins studied here are shown in Figure 4 a and b.

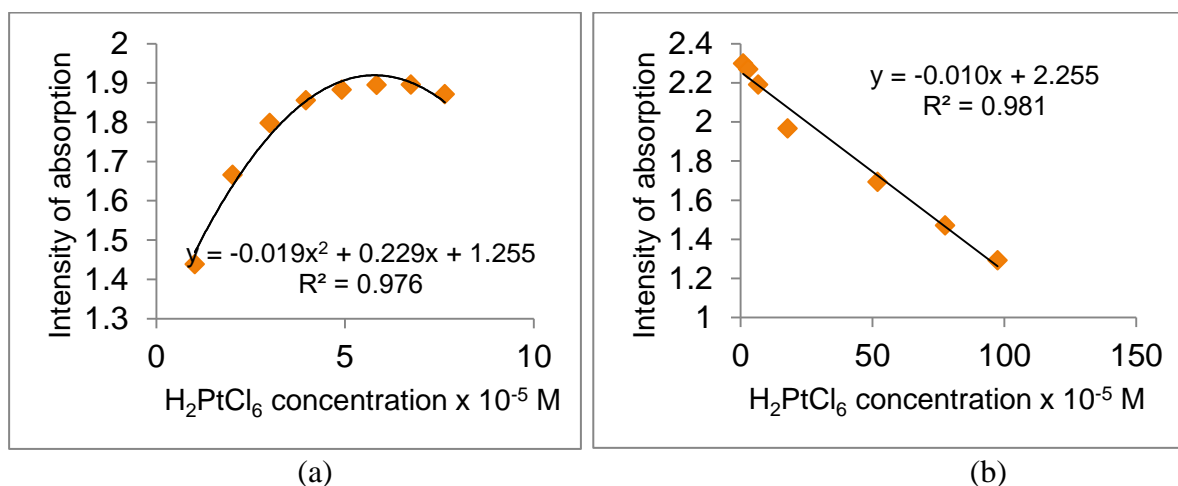


Figure 4. Polynomial a) and linear b) dependence between the intensity of absorption read at Soret maximum wavelength and the H_2PtCl_6 concentration in case of using Zn(II)-tetrakis-pyridylporphyrin (a) and Zn(II)-5-pyridyl-10,15,20-tris-(3,4-di-methoxy-phenyl) porphyrin (b)

It can be observed that the plateau is obtained by Zn(II)-tetrakis-pyridylporphyrin at a very low concentration of hexachloroplatinic acid up to 5×10^{-5} M, but the interference between the unsymmetrical Zn(II)-5-pyridyl-10,15,20-tris-(3,4-di-methoxy-phenyl) porphyrin and H_2PtCl_6 has a twentyfold wider domain up to 100×10^{-5} M.

The removal capacity of Pt colloidal particles from solution can be calculated according to the formula [4]:

$$\text{Removal capacity (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100$$

In our case the removal capacity is 84.867 % for Zn(II)-tetrakis-pyridylporphyrin and 98% for Zn(II)-5-pyridyl-10,15,20-tris-(3,4-di-methoxy-phenyl) porphyrin, result that is surprising, due to the large number of basic molecules of the Zn(II)-tetrakis-pyridylporphyrin.

The obtaining of the desired Pt nanoparticles from the complexes that were formed with Zn-metalloporphyrins, was done in each case, by adding 4.55 mL of NaBH₄ solution in water ($c = 7.077 \times 10^{-3}$ M) (a tenfold more concentrated NaBH₄ solution than the expected concentration of Pt) to 5.5 mL of each complex solution. When NaBH₄ was added under stirring, almost instantly an intense brown colloidal solution was formed. After a few seconds, the particles of Pt were observable with the naked eye.

Conclusion

Two Zn-metalloporphyrins, both containing pyridyl groups, were tested regarding their capacity to complex hexachloroplatinic acid resulted in leaching solutions after hydrometallurgical processes on spent automotive catalysts. Although it was believed that the bigger number of pyridyl groups will be a benefit for complexation, it was surprisingly found that the loss of planarity, the steric and electronic inductive donor influences from the surrounding -OCH₃ groups determine a better coordination with the hexachloroplatinic acid for the unsymmetrical Zn(II)-5-pyridyl-10,15,20-tris-(3,4-di-methoxy-phenyl)-porphyrin that had an excellent removal capacity of 98%, based on axial coordination on Zn atom.

Acknowledgements

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