Synthesis and PM6 semiempirical studies of self-assembled Ni, Pd and Pt supramolecular polygons

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ABSTRACT:
In this work self-assembled complexes with novel architectures that possess metal centers of the same group M = Ni, Pd and Pt were prepared. The supramolecular polygons were synthesized from a common metal complex type: [M(dppe)Cl] (M: Ni, Pd and Pt, dppe = diphenylphosphine), and characterized experimentally by UV, IR, FT-Raman, elemental analysis, 1H NMR, 2P-NMR and by PM6 theoretical studies. The synthesis was performed of interest complexes type: [M(dppe)(TOF)] (M: Ni, Pd and Pt), with silver trifluoromethanesulfonate (Ag·TOF). Finally the self-assemble process of the polygons were made between the organic linker 4,4'-bipyridine and the interest complexes, which act as edges and corners in the polygons structures respectively.

PM6 calculations performed for the supramolecular complexes showed that the complex is cationic ([M(dppe-4,4'-bipy])3+ (M: dppe-4,4'-bipy)), and neutral complexes ([M(dppe)(TOF)]4-4,4'-bipy), both in gas phase and in solution (CH2Cl2, CDCl3 and CHCl3). The results show that for the three metals in the gas phase, the formation of triangles was favored compared to the formation of squares. However by including the solvent effect, the squares with Ni and Pd are more stable than the respective triangles, whereas for the Pt the triangle is more stable than the corresponding square. Based on the integrals (3F + 2P-NMR) the ratio of formation of the polygons for palladium was 72% square and 28% triangle. For platinum 74% triangle and 26% square and for nickel 100% square. The theoretical calculations were in agreement with the experimental results.

Keywords: supramolecular polygons, Ni, Pd, Pt squares, self-assembly, PM6 semiempirical studies.

INTRODUCTION:
Metal organic Polygons and polyhedra (MOP) are organic compounds, generated from di- and tri-topic ligands with metal centers (generally transition), which have two or more coordinate sites available with a predefined geometry (Figure 1). These structures present many novel applications such as nanoreactors, molecular nanosensors, host-guest chemistry, synthesis of nano particles, nano catalysis, molecular recognition and nanoelectronics, among others.

Many factors affect the viability of the self-assembly process in supramolecular polygons, such as: the weak links, enthalpic favorability, thermodynamics viability, concentration, solvent, the lability of the metal-nitrogen bond, the angle and strength of the chelating ligand, the nature of the metal ion, the temperature, the kinetics and thermodynamics of process, and the bite angle.

In many metallo-supramolecular systems equilibria between two or more species establish, because there is no clear preference for one of them from a thermodynamic point of view. Some authors who have studied these equilibria are Ferrer and Würthner among others. Which have been reported obtaining highly symmetric two species in equilibrium (triangle-square).

METHODOLOGY:
Figure 2 describes the overall methodology for the final self-assemblies, between complexes type [M(dppe)(TOF)] (M: Ni, Pd and Pt) with 4,4'-bipyridine, which generated the formation of supramolecular polygons. All complexes and polygons were characterized by spectroscopic techniques, which are supported by semiempirical theoretical studies PM6.

RESULTS AND DISCUSSION:
During the process of self-assembly of supramolecular polygons, trifluoromethanesulfonate ion (CF3SO3−) are displaced by 4,4'-bipyridine, and are located outside the inner coordination sphere acting as counter ions, balancing the positive charges of the metal centers in the structure. Figure 3 presents the 31P NMR spectra of supramolecular polygons obtained. The signals correspond to the phosphorus atoms of dppe coordinated to the metal centers in the supramolecular structures. These signals shift into high field present due to the structural proximity present with the nitrogen atoms of the 4,4'-bipyridine, which are quite strongly electronegative atoms.

For the case of nickel a single signal located at 30.57 ppm (Figure 3-A) is observed due to the presence of coordinated phosphorus atoms in a unique chemical environment which corresponds to a square supramolecular. For the palladium macrocyclic species (Figure 3-B) two signals located at 66.69 ppm and 68.20 ppm are shown, indicating the presence of two different species, which confirmed the existence of an equilibrium between two different species (triangle-square). Therefore previous studies by Ferrer et al. revealed that in a similar supramolecular triangle-square equilibrium the low field signal corresponds to the square while the high field signal corresponds to the triangular species. These shifts arise from variations in the N-M-P bond angle.

Similarly, the spectrum of the platinum macrocyclic species (Figure 3-C) presents two signals at 37.37 ppm and 35.67 ppm, due to phosphorus atoms coordinated in two supramolecular species (triangle-square), which are in equilibrium.

In addition, the spectrum shows two symmetrical signals to each phosphorus signal, which correspond to 3P satellites. These satellites are generated, due to the susceptibility of the platinum isotope 195 in NMR and by differential coupling that occurs between them with each phosphorus signal.

To compare the stability of the square and triangle complex, from the PM6 from the heats of formation calculated H° to PM6 level, H0(square)-H0(triangle) was calculated. H0 values and ΔH° for the free molecule (gas phase) and CH2Cl2 and acetone respectively, are very close to the value of 8.4 Kcal/mol reported in DMF for similar complexes of Pt4. The results presented show that both the gas phase and in solution ΔH° is positive, which means that the square supramolecular is more energetically favored than the triangles, due to the strain generated in the triangular species due to the distortion of the geometry in the 4,4'-bipyridine. It is also observed that ΔH°(Ni)-ΔH°(Pd)-ΔH°(Pt), regardless of the medium. From these theoretical results, it can be concluded that nickel centers favor formation of squares, whereas in Pt centers, the triangles formation is favored.

CONCLUSION:
Table 1 shows the stability for palladium (II) and platinum (II) were studied. Reporting for palladium macrocycles the preponderance of square over the triangular species, with a percentage of 72% and 28% respectively. While in the equilibria of species of platinum (II), formation of the triangular species was favored with a ratio of formation of 74% and 26% for the square. In the case of nickel was obtained 100% square.