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Efficiency in transporting molecular oxygen to iron(II) complexes with ligands type tri (2-pyridylmethyl) amine substitution aromatic in (α) position by a mechanism that mimics biological oxidation

Dr. Nasser Thallaj

Faculty of Pharmacy. Al Rasheed Private University. Damascus, Syria

ABSTRACT

Biological mimicry of the oxidation process of the active sites of iron proteins leads to the formation of peroxides, specifically oxygenated water, where the latter is a strong and highly satisfactory oxidizing agent, characterized by non-toxicity and low cost. In many cases, nature employs molecular oxygen for oxidative processes, particularly under extenuating conditions. Iron complexes with tris(2-pyridylmethyl)amine ligands have been studied to mimic the biologically active sites and prove their vital importance.This paper studies the possibility of obtaining iron(II) complexes with aromatic bonds of the tri-type (2-pyridylmethyl)amine on the alpha site of the nitrogen atom with testing the activity towards molecular oxygen for one complex selected from the synthesized complexes.

Key words: Biomimetics, tri (2-pyridylmethyl)amine, activation of molecular oxygen, iron(II).

Introduction

The mediation of the process of transferring oxygen to an organic substrate has been well studied in biology and is realized. This process is carried out by enzymes (proteins with metal centers), for example cytochrome enzymes. P-450 (cytochrome P-450) (heme iron-containing centers) or non-haemic enzymes, as an example, are methane monooxygenase [1]. These reactions can be carried
out using molecular oxygen. Another well studied enzyme in biological systems is tryptophan hydroxylase, which catalyzes a key step in serotonin biosynthesis and plays important roles in the circadian rhythms [2-8]. This reaction is achieved using molecular oxygen, in which case the molecular oxygen must be stabilized and then a functional class of hydropyroxo is formed, after which the O-O bond is broken. In the last case, after cleaving the bond, a very effective class is formed, metal- oxo [9-11]. According to the illustrated mechanism (Figure 1), this mechanism is a biological mechanism for the activation of molecular oxygen.

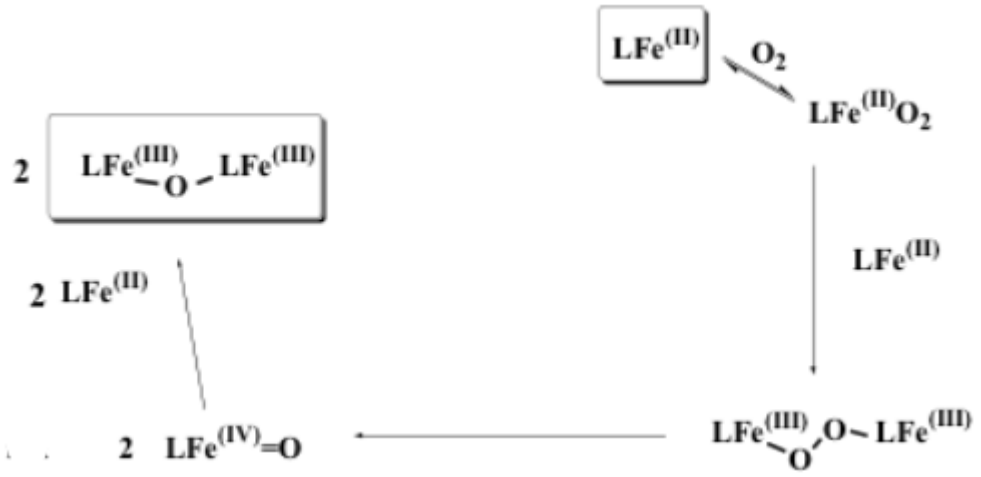


Figure 1: shows the stages of interaction of biologically active sites with molecular oxygen according to a biological mechanism.

Iron complexes with a type of tetradental or tetradental ligands known as tetradent-TPA or tris(2-pyridyl methyl)amine (TPA) and their multifunctional derivatives have been well studied in recent years. Some of them gave functional analogues to some non-hemian iron enzymes, which fall within the domain of activation of molecular oxygen [10-12] taking into account that in most cases hydrogen peroxide (oxygen water) is used as an oxygen-giving agent [11-22].

Although molecular oxygen is used, it should be noted that it only reacts with iron(II), which is associated with the substrate and which plays a role in activating the metal such as catechols and thiols [22-26] (Catechols and Thiols), for example. In the last ten years, iron(II) complexes with TPA-type conjugates with multiple substitutions have been extensively studied [27-31].

The substitution in the alpha-site, for the nitrogen atom, leads to a complex process for the metal in a four-tooth or three-tooth pattern, depending on the type of mineral salt used and according to the type of ligands and functional groups present on it.

A group of these ligands have been synthesized and the preliminary study of their complexes and their effectiveness with molecular oxygen and the effect of substitutions on efficiency and complexity pattern. The organic synthesis of these bonds, and then complexing some of them with binary iron, and these complexes were subjected to special reactive conditions, and the activity was tracked by several techniques, including ultraviolet spectroscopy and NMR spectroscopy of the complex of the paramagnetic type.

Synthesizing ligands:

A group of ligands of the type (TPA) mono-substituted were synthesized, whereby substituents were selected that activate this type of complex.
(PhCH2OH, PhCH2NH2, PhNH2, PhOH, PhCN, PhCHCH2)

The above-mentioned functional groups were selected based on a prior study of the concepts of molecular engineering and biomimetic of biologically active sites, taking into account the improvement of the effect of the added groups on the activity of these functional centers which are synthesized to mimic the biologically active centers.

The synthesis was done in multiple stages (Figure2) with the selection of the Suzuki coupling Synthesis to add new and diverse groups to the pyridine ring as it gives a very good yield.

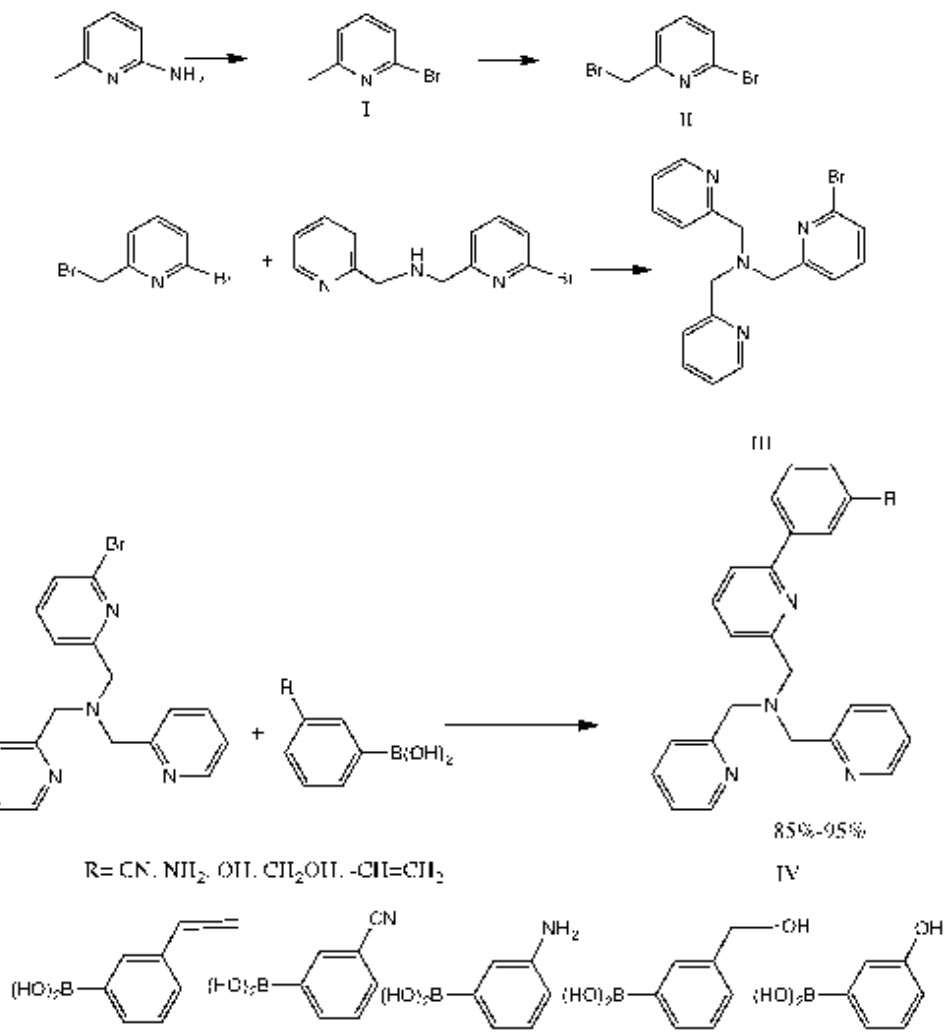


Figure2: I) :Br2, HBr, NaNO2, H2O, 0°C. II): NBS, dibenzoylperoxyde, CCl4, reflux 15h. III): Na2CO3 inCH3CN reflux 16h. IV) $Pd(PPh)_4$, Toluene, reflux, 25h, 105C

This research attempts to prove the possibility of activating molecular oxygen by iron-II complexes with tris(2-pyridyl methyl)amine (TPA) ligands with ligands pattern. They form penta-coordination or hexa-coordination complexes, which vary in effectiveness with molecular oxygen. This research aims to prove that iron (II) complexes with tris(2-pyridyl methyl)amine (TPA) ligands are able to activate molecular oxygen and trace the kinetics of this reaction by means of different spectrophotometers.

- Conducting a simple test for the transfere of molecular oxygen after activation with this type of complexes for an organic substrate, ie, testing the mediation of these complexes for the process of transferring molecular oxygen.

Determining the optimal conditions for the catalysis process using molecular oxygen and trying to improve the reactive conditions and laying the foundations for the development of these links to serve this process. The importance of this research lies in the biological simulation of the active sites in the enzymes, which provide nice interactive conditions using air oxygen, which can be developed in the future by binding either to a protein of the electron-carrying type or to metallic nanosurfaces so as to take advantage of the advantages of nano-mediating, and on the other hand it allows implanting these complexes on the surfaces of A mineral with a source of electrons, which allows the return of ternary iron resulting from the oxidation process to iron binary. This study is based on the principle of defining the conditions that must be improved in the bonds in terms of the space condition in terms of controlling the type of pentagonal or hexagonal bonding and the electronic condition in terms of determining the withdrawing groups and the electron-giving groups that must be added to improve the interactive conditions. On the other hand, the effect of temperature on the complexity pattern was investigated. These bonds were synthesized by multi-stage organic synthesis and various techniques were used in this study such as separating columns for post-reaction purification, NMR spectroscopy, near-infrared ultraviolet absorption spectroscopy, and analysis by gas-phase chromatography. Various factors affecting were studied. on interactive and compare it to some of the results found on the scope of the research published in this regard.

General method for forming iron (II) complexes:

These associations are complicated with the anhydrous iron (II) chlorine salt; given that the anhydrous iron (II) chlorine salt is a bright white solid.
The complex reaction continues for five hours using acetonitrile (CH3CN) or tetrahydrofuran (THF), taking into account the good and modern distillation of the stores, meaning the absence of water in them. :

$$L + FeCl_2 \xrightarrow[\text{Argon/ 5 h}]{\text{THF Or } CH_3CN} LFeCl_2$$

After drying and converting the prepared complexes to a solid state, they become soluble compounds such as acetonitrile (CH3CN) in preparation for its study using the following techniques:

• Ultraviolet Absorption Spectrophotometer The device used is of the type: (Varian CARY 05E UV-vis-NIR)
• Nuclear magnetic resonance of the type of repulsive magnetism The device used is of the type: (Bruker AC 300 fonctionnant à 300.1300 MHz.)

Studying and characterizing the complexes of some of these links using Spectrum UV-visible spectroscopy.

Iron Dichloride (FeCl2) salt complexes with this type of ligands:

- CNPhTPA

It gives two strong and distinct absorption bands at the wavelength (256.5 nm, and λ=283.6 nm).

- CH2CHPhTPA

In the case of complex with CH2CHPhTPA, the absorption bands are at
(270.5 nm, λ=300.0 nm).

- NH2PhTPA

As for the case of NH2PhTPA, these bands are (260.0 nm, λ=290.0).

Double bands are a band that describes the conjugation of phenyl groups substituted with the pyridine ring back in the transition $\pi \rightarrow \pi^*$. As for the weak absorption band, which is located at λ=389.0 nm, 383,0 nm and 323,0 nm, respectively, it describes the charge transfer from the d-orbtals of iron to the π orbitals of pyridine **Fe→L**, i.e. the charge transfer from the metal to the ligand (Figur3).

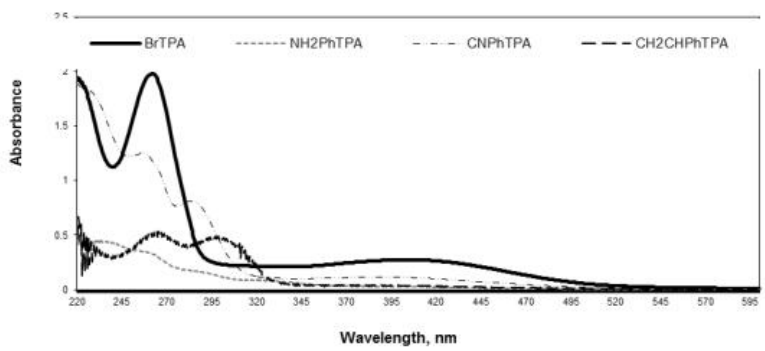


Figure 3: UV spectroscopy of the above complexes

In some cases, the change of UV absorption spectroscopy with the change of temperature strongly indicates the change of the bonding from pentagonal to hexagonal and vice versa or the formation of binuclear complexes, so the UV absorption spectroscopy of the complex (CNPhTPAFe(II)Cl2,) at various temperatures was studied, which indicates Figure 4. Absorption spectroscopy does not change with temperature change.

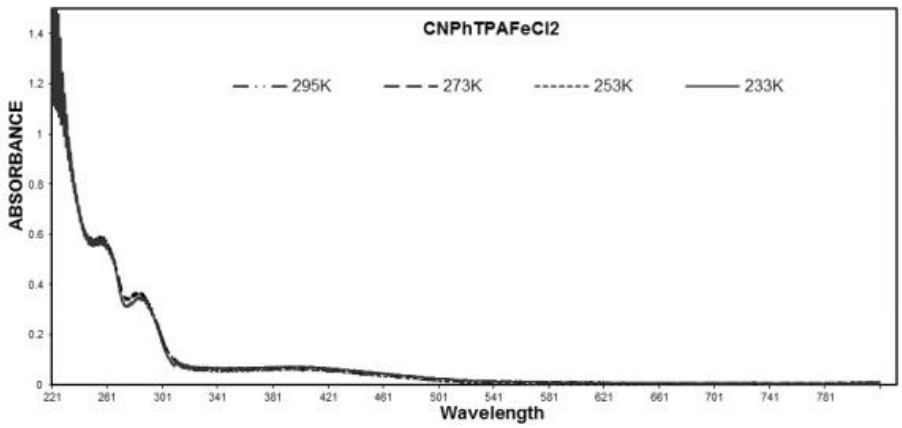


Figure 4: Ultraviolet absorption spectroscopy of the complex (CNPhTPAFe(II)Cl2,) at various temperatures.

All the complexes formed from ligands and iron(II) have direct magnetism and this type of compound has been studied for many years by NMR spectroscopy.

In general, the mechanism of the effect of the nucleus of the repulsive magnetic element is observed in direct contact through the chemical bond, and this is the result of the dipole effect within the same class. This type of spectroscopy allows to study the state of the spin of the mineral center and its effect on the displacement of the resonance significantly. Two complexes have been previously studied, namely BrTPAFe(II)Cl2, Br2TPAFe(II)Cl2, where an important paper was published [25-40], which enabled them to be taken as reference compounds to determine the stereoscopic geometry The complex is either pentacovalent or hexagonal depending on the shape of the signals in this type of spectrometer and by making use of the UV absorption spectroscopy as shown in Figure 2. The comparison between the signal forms of these two complexes and two of the ligand complexes that were synthesized in this research (BrTPAFe(II) (Cl2, Br2TPAFe(II)Cl2, CNPhTPAFe(II)Cl2, NH2PhTPAFe(II)Cl2) The possibility of predicting the stereoscopic shape in the liquid state of the two complexes, where the linking of the signals shapes for the BrTPAFe(II)Cl2 complex indicates that it is a hexacoordination) while a complex (By comparing the spectroscopy of the new complexes with the two reference complexes, we find that the spectra signals are close to the hexagonal in terms of the resulting peaks and their shapes, as shown in Figure 5 and Figure 6.

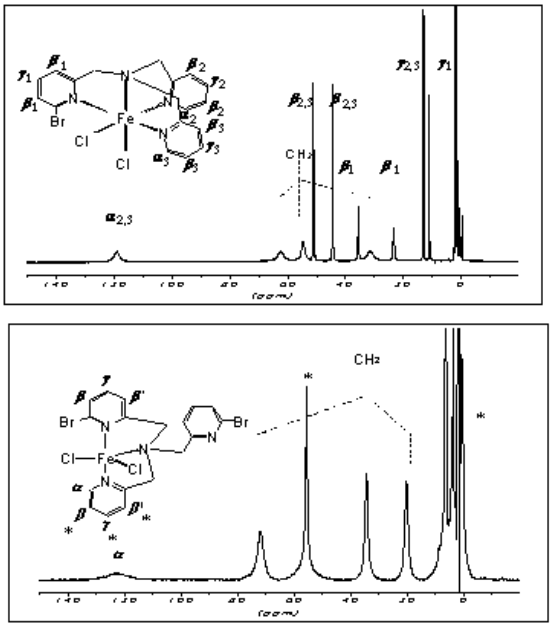


Figure 5: NMR para magnatic spectroscopy of the two reference complexes and the bonding pattern of BrTPAFe(II)Cl2, Br2TPAFe(II)Cl2.

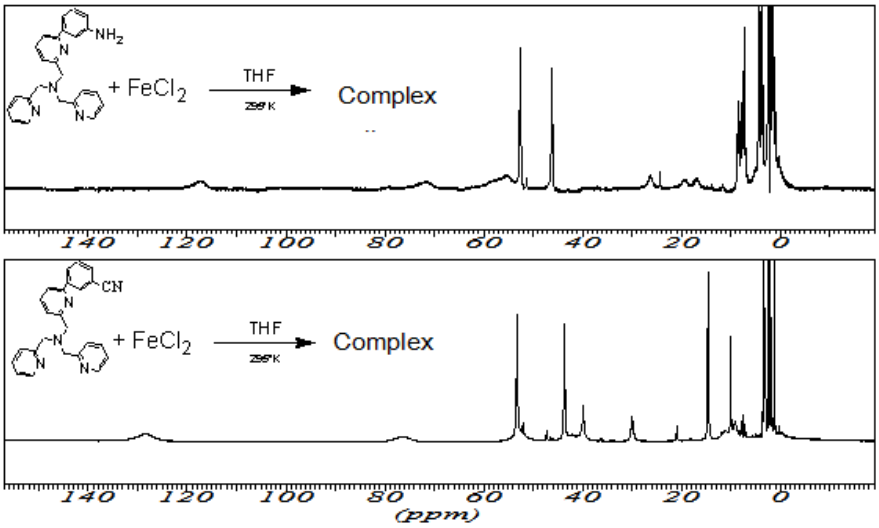


Figure 6: NMR para magnatic spectroscopy of the complexes CNPhTPAFe(II)Cl2, NH2PhTPAFe(II)Cl2.

An example study of the effectiveness of this type of complex with molecular oxygen:

We take as an example of this complex reactivity, CNPhTPAFe(II)Cl2, because the substituent on the ligand is electron-withering, which enhances the Lewis acidity of the metal center [25-55]. We inject molecular oxygen into the measurement cell, which is in an anhydrous medium and in an atmosphere of inert argon gas. We measure before injecting oxygen and after 30 seconds. Then we measure at a rate of once every 15 minutes. We note the change in the shape of the spectrum and its evolution, noting that the reaction ended within an hour as shown in the spectroscopic study. The same Conditions in two types of spectrometers (Fig. 7) and (Fig. 8) as shown by the resonant magnetic resonance spectroscopy of the reciprocal magnetic type, which shows the absence of all peaks from the repulsive magnetic region and its displacement to the reversible magnetic region when interacting with molecular oxygen, which is traditionally described forming the µ-oxo species.

The formed variety is of the µ-oxo type. This type of species has an absorption spectrum by ultraviolet spectroscopy at the wavelength λ = 0, 350 nm, where we noticed the formation of the absorption spectrum at this value, while we do not notice changes in the location of other peaks.

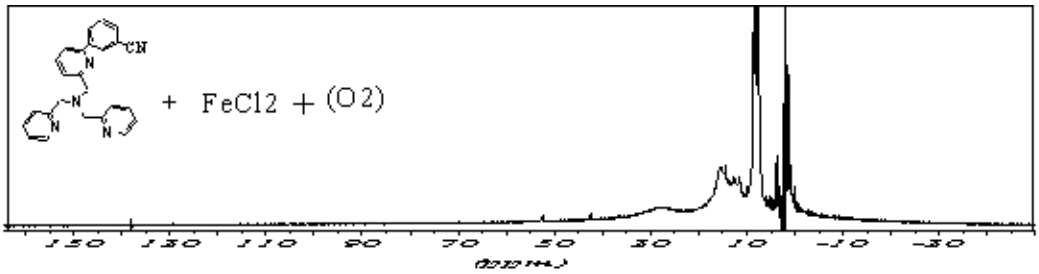


Figure 7: shows the reaction of the complex CNPhTPAFe$^{(II)}$Cl2 With molecular oxygen, and formed the species metal-Oxo (µ-oxo).

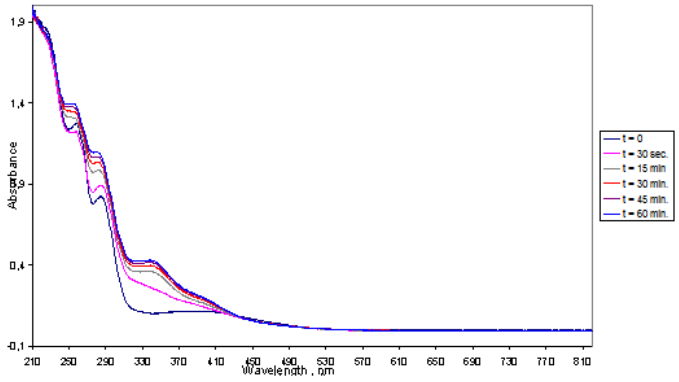


Figure 8: Reaction measurements with molecular oxygen using UV-vis absorption spectroscopy.

- Study to test the reaction of molecular oxygen with a substrate:

The mechanism of interaction of this type of complex with molecular oxygen (Fig. 1) shows that the quaternary iron should be formed as a Fe(IV)-oxo intermediate state. This state represents the active class by the molecular oxygen transfer process by the biological mechanism that we seek to simulate. We conducted a test of converting cyclohexane to cyclohexanone using two models of the complexes that were prepared, and a test was conducted for the iron(II) salt and the (III) iron salt to know the role of the ligands in the efficiency of oxygen transfer to the substrate. FeIII/FeII. Zinc amalgam was used to secure the process of reducing ferric iron to FeIII/FeII binary.

The process of determining the output and calculating the yield was done by gas phase chromatography (CPG).

[cyclohexanone] =1.2[acetophenone]*Air(cyclohexanone)/Air(acetophenone)

TON=[cyclohexanone]/[catalyst]

	$NH_2PhTPAFeCl_2$	$CNPhTPAFeCl_2$	$FeCl_2$	$FeCl_3$
TON	=13	=40	0.24	0

These results indicate the effectiveness of these complexes towards molecular oxygen in terms of activation and the interaction of the activated class with a substrate, and the absence of this activity completely for the iron(II and III) salts.

Result :

2-Bromo-6-Methylpyridine[38]

27 g (250 mmol) of 2-amino-6-methylpyridine dissolved in 150 mL of hydrogen bromide, reduce the reaction temperature to 0℃ using an ice and table-salt mixture bath The mixture is stirred with an outboard motor of the type stirred mixer The forearm is that the mixture becomes very viscous, and the stirring process with this type of mixer provides a good thermal homogeneity process, which the stirring process using known magnetic motors does not provide. 38 milliliters of bromine are added drop by drop to the reaction mixture during 40 minutes, the temperature being maintained at 0°C and not exceeding 0°C. 40 g (623 mmol) of sodium nitrite are dissolved in 100 ml of distilled water and slowly added to the reaction mixture over a period of 60 minutes. At the end of this stage, the reaction has been completed, and then the reaction medium is modified using a solution of 80 g of sodium hydroxide in 100 ml of distilled water and the product is extracted several times using ether. Distillation of the product under reduced pressure of 15 mmHg The resulting cut between a temperature of 93-95 degrees Celsius is the compound, which is a colorless oil that crystallizes upon cooling to zero degrees Celsius.

NMR^{1}H, ($CDCl_3$, δ, ppm) 7.44-7.41-7.38, (1Hγ, t,J1= 9 ;J2=9) ; 7.28-7.26 (1Hβ, d, J=6); 7.10-7.07 (1Hβ',d, J=9); 2.52, 3H, s(CH_3).

2-**Bromo-6-Bromomethylpyridine[39-41]**

Dissolve 4 g (23.3 mmol) of 2-bromo-6 methylpyridine in 200 ml of carbon tetrachloride

4.5 g (25.3 mmol) of N-bromosuccinimide is added, then 0.93 mmol of benzoyl peroxide is added as the initiator of the radical bromination reaction. The reaction is carried out by back-distillation at 90 ℃ for 5 hours and under the influence of a mercury lamp throughout the reaction period. At the end of the reaction, the solution is evaporated, then the product is dissolved with toluene, and the separation is done using column chromatography technology using silica, and we have 2-bromo-6-methylpyridine, which is a white solid with a yield of approximately 55%.

NMR^{1}H : ($CDCl_3$, δ, ppm) : 7.7-7.3, $3H_{arom}$, m; 4.4, 2H, s.

2-Bromo 6-aminomethyle pyridine[32-47]:

Dissolve 7.04 g (29.7 mmol) of 2-bromo-6-bromomethylpyridine in 50 ml of (DMF) and add to it 11.8 g (63.9 mmol) of potassium phthamidamide and 6.38 g of sodium bicarbonate (73.7 mmol) the mixture is placed by reflux distillation for 6 hours and then cooled to room temperature and the white solid is removed by filtering and then the solution is evaporated and distilled water is added gradually until it forms a white precipitate and then filtered the solid substance, which is a phthal amide derivative, this compound is treated B 150 milliliters of hydrogen bromide 48% and the mixture is placed by reflux for 15 hours, the product is cooled to precipitate phthalic acid, which is separated and 10 molar sodium hydroxide solution is added to the remaining solution with cooling to reach an alkaline medium pH 10, and then the compound is extracted with ether (diethyl ether).) more than once and the product is dried using anhydrous magnesium sulfate, then filtering and evaporation of the solution, we get 2-bromo-6-aminomethylpyridine with a yield of 58%.

NMR^{1}H: ($CDCl_3$, **δ** , ppm): 7.6 (dd,1H), 7.3-7.1 (m, 2H), 4.0 (s, 2H), 2.0 (br s).

Bis(pyridine-2-ylmethyle)amine (DPA)[39-46]

Dissolve 5 g (39.2 mmol) of picolillyl chloride dissolved in 120 mm L of ethyl alcohol and add to it 8.84 g (81.8 mmol) of 2-aminomethylpyridine. The mixture is placed for 12 hours by reflux distillation. At the end of the reaction, an aqueous solution of potassium carbonate is added. Then dichloromethane is added, the organic phase containing the desired compound is separated, and the organic phase is dried by anhydrous magnesium sulfate, and then the magnesium sulfate is separated by filtering and evaporation of dichloromethane.

The compound is separated by distillation under reduced pressure 1-2 mmHg using a low pressure distillation device, which is a multi-ended frosted device (cow's udder), where it is separated at a temperature of 45-55 degrees Celsius, which is 2-aminomethylpyridine, which is the raw material that can be reused. As for the required compound, it distills at a temperature ranging between 139-141 degrees Celsius, and it is a dipyridine 2-methylamine (DPA) with a yield of 80%, and it is a transparent, yellowish oily compound.

NMR^{1}H: ($CDCl_3$, δ , ppm): 7.6-6.8, (m, $6H_{arom,}$); 8.5, (dd $2H_{arom}$); 3.82, (s, 4H).

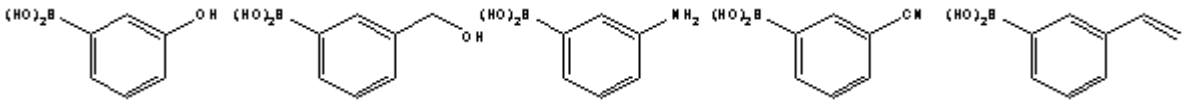
(2-bromo-pyridine-6-ylméthyle)Bis(pyridine-2-ylméthyle)amine (BrTPA) [41-43]:

Dissolve 43.2 g (12.2 mmol) of bis-methylpyridine (DPA) in 150 ml of ethanol, add 3.088 g (12.3 mmol) 2-bromo-6-bromomethylpyridine, and add 4 g of potassium bicarbonate to the solution. The reaction mixture for 20 hours by reflux distillation at 90 ° C, the product was dried with anhydrous sodium sulfate, and the solid was separated from the liquid by filtering. After evaporating the solution, the product was obtained by extracting it with pentane cooled to a temperature (-20 degrees) and by evaporating the pentane, we obtained the product in the form of needle crystals. Bright white with a yield of 45%, knowing that these crystals are transformed at room temperature into a viscous oil.

NMR^{1}H : ($CDCl_3$, **δ** , ppm) 8.54, $2H_{arom,}$ d; 7.62-7.16, $9H_{arom}$, m; 3.88, 6H, s.

TPA-mono substitution [44-49]:

These compounds are prepared by the Suzuki reaction using homogeneous catalest of palladium and a variety of Boronic acids as shown below.



Dissolve 800 mg of Br-TPA (2.17 mmol) with toluene treated by degassing to ensure the absence of oxygen, as this medium is sensitive to the presence of oxygen and uses equal stoichiometric equivalents (ie equivalent to equivalent) of the corresponding boronic acid, then add 7.2 milliliters of a solution Freshly prepared sodium carbonate (21.2 grams dissolved in 100 milliliters of water) and the intermediate Pd(PPh3) is added. The reaction is carried out in an inert atmosphere of argon gas for 25 hours by reflux distillation. The solution is evaporated, then the product is dissolved in dichloromethane, washed several times with a solution of sodium carbonate, and then dried. Using anhydrous magnesium sulfate, the solution is evaporated, and the resulting compound has a yield of 80%.

HOPhTPA :
NMR : H^1, ppm, CDCl3: δ 8.50 (d, 2H, Hα) 7.65-7.00 (dd, 9H) 6.83 (dd, 2H) 3.98 (s, 4H, CH2) 3.92 (s, 2H, CH2)

$HOCH_2$PhTPA:
NMR : H^1, ppm, CDCl3: δ 8.50 (d, 2H, Hα) 8.1-7.1 (m, 11H) 4.8-4.6 (s, 2H, CH2OH) 3.9-3.88 (s, 2H, CH2) 3.88-3.86 (s, 4H, CH2).

NH_2PhTPA:
NMR : H^1, ppm, CDCl3: δ 8.50 (d, 2H, Hα) 8.1-7.1 (m, 11H) 6.65(m,2H)3.95(s,4H CH2) 3.98(s, 2H, CH2).

CNPhTPA:
NMR : H^1, ppm, CDCl3: δ8.50 (d, 2H, Hα) 8.44-8.30 (m, 1H) 8.25-8.20 (m, 2H) 7.93- 7.05 (m, 11H) 4-3.94 (s, 2H, CH2), 3.94-3.88 (s, 4H, CH2).

Discussion and conclusion:

Using ultraviolet spectroscopy, we have studied examples of iron (II) complexes with this type of ligand (TPA-PhX) and nuclear magnetic resonance spectroscopy of two previous complexes.

(CNPhTPAFe(II)Cl2, NH2PhTPAFe(II)Cl2) in addition to comparison with previously studied reference compounds in depth (BrTPAFe(II)Cl2, Br2TPAFe(II)Cl2,), so that it was possible to predict the geometry of the complex in terms of the pentagonal or hexagonal bonding pattern in the liquid state. .

We subjected one of these complexes (CNPhTPAFeCl2) to an activity test with molecular oxygen in the absence of a substrate to confirm the ability to activate molecular oxygen. The reason for choosing this complex lies in the fact that the cyan group on the aromatic substituent enhances the property of Lewis acid on the metal center as it is a drag group. The result was positive, as the reaction was followed by multiple measurements by ultraviolet spectroscopy, and it was found that the reaction ended within 60 minutes.

With the presence of a substrate such as cyclohexane, the oxidation reaction test was conducted using molecular oxygen and the transformation from cyclohexane to cyclohexanone using this type of complex.

This study showed that the presence of functional groups on this type of bond improved well in the properties and activity of their complexes (which is due to the electronic effect) with molecular oxygen. The association of this type of complex with protein materials carrying electrons allows the conversion of ternary iron after the reaction to iron, which enables the design of systems that allow biological simulation of oxidizing enzymes that interact under gentle conditions and using air oxygen and allows the development of inexpensive industrial processes in the long run.

Linking these complexes to nanoscale surfaces allows the preparation of a nano-catalysis for many oxidation processes or the formation of what is known in the elemental analysis as oxygen captors, and linking them to solid surfaces allows the formation of what is known as electro-catalysis or mediation. on the surfaces of the tracks.

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