



ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(1):124-127
(<http://derpharmachemica.com/archive.html>)

Synthesis, characterization and spectroscopic studies of Iron (III) and Copper(II) complexes of α -hydroxyl phosphonate

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ABSTRACT

Previous studies show that the phosphate groups play a role important in the complexation process as a whole more effective donor than carboxylate groups. The presence of the aromatic ring increases the power of complexing of these molecules. We present here a spectrophotometric method for the determination of two complexes $[M(L_1)_nH_2O]$ where $L_1 =$ dimethyl (hydroxy(phenyl)methyl)phosphonate and $[M(L_2)_nH_2O]$ where $L_2 =$ diethyl (hydroxy(phenyl)methyl)phosphonate, the procedure is based on the chelation of the ligand with Fe (III) to form a red complex and Cu (II) to form a yellow complex at room temperature which absorbs maximally at 405 nm and 308 nm and Beer's law is obeyed over the concentration range of 2-27 mg/ml. The IR spectroscopy revealed that iron and copper ions are coordinated through the phosphoryl (P=O) and hydroxyl group (O-H) of the α -hydroxyl phosphonate.

Keywords: Iron (III), Copper (II), spectrophotometry, complex, α -hydroxyl phosphonate.

INTRODUCTION

Considering the enormous significance of organophosphorus compounds in nature, it is surprising that naturally occurring phosphonates, which contain a C–P bond, have only been known since 1959 when (aminoethyl)phosphonic acid was isolated from sheep rumen [1]. Since then, numerous compounds of this class have been isolated, synthesized, and tested for their biological activity [2].

α -hydroxyl phosphonates exhibit a variety of interesting and useful properties that make them attractive as herbicides, antibiotics, pesticides, antiviral and anticancer agents [3-7].

On the other hand, phosphonates are brought into contact with +II and +III toxic metal ions during their use. Upon disposal, metal-phosphonate complexes persist long enough to significantly alter toxic metal adsorption/desorption behavior. Ultimately, +II toxic metal ions are displaced from their phosphonate complexes by the dissolution of Fe(III) and Cu (II)-containing minerals [8].

Phosphonate functional groups have appeared in the structures of a growing number of manufactured chemicals. Phosphonate-based chelating agents are used to prevent the formation of undesirable precipitates, and to protect others from dissolution. Such chelating agents are used to depress free metal ion activity and to increase total metal ion concentrations [9].

Previous studies show that the phosphate groups play a role important in the complexation process as a whole more effective donor than carboxylate groups. The presence of the aromatic ring increases the power complexing of these molecules. S. Lacour and al [10] determined the stability constants of complexes formed by HEDP and ATMP two phosphonic acids with metal cations, Al (III), Cr (III) and Fe (III). In this paper we present synthesis, characterization and spectroscopic studies of new Fe(III) and Cu (II) complex with two ligands L₁ and L₂.

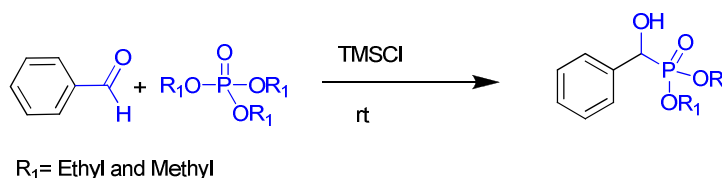
MATERIALS AND METHODS

Experimental

The IR spectra of the powder ligand complex with iron that have been registered in an organic solvent (chloroform) using a Shimadzu infrared IR spectrometer Type and UV-Visible spectra were recorded using a spectrophotometer such Analytikjena SPECORD 200 plus dual beam. The measurements were performed in a quartz cell of 1 cm optical path between 200 and 800 nm on the concentration 10⁻³M at room temperature for iron(III) and Cu(II) complex. The structures proposed for iron(III) and copper(II) complexes of α -hydroxyl phosphonate are shown in fig.1.

Synthesis of ligands

The following procedure [11] has been used in the preparation of ligand L₁ and L₂ (scheme 2)



Scheme 1: Synthesis of ligands

Synthesis of Fe(III) – mixed ligand

A solution of FeCl₃·6H₂O (27 mg, 10mmol), L₁ and L₂ (21.6 mg, 10mmol) in chloroform (10 ml) was stirred for 15 min after evaporation a red powder is obtained. The yields of the complexes were almost quantitative.

Synthesis of Cu(II) – mixed ligand

A solution of CuSO₄·5H₂O (27 mg, 10mmol), L₁ and L₂ (12 mg, 10mmol) in chloroform (10 ml) was stirred for 15 min after evaporation a yellow powder is obtained. The yields of the complexes were almost quantitative.

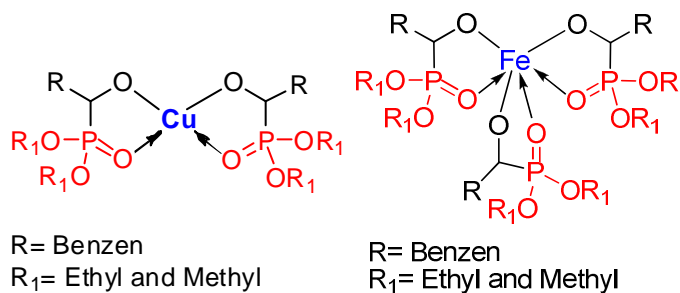


Figure 1: proposed structures

RESULTS AND DISCUSSION

FT-IR Spectra

The decrease in the intensity of bands 3263 cm⁻¹ in the spectra of the complex iron (III) and 3447 cm⁻¹ in the spectra of the complex Cu(II) indicate the absence of the phenolic OH bond relative to the ligand spectrum which is a broad band of 3500-3000cm⁻¹. The spectra show an absorption band located at 3050-3000 cm⁻¹ attributed to the vibrations of aromatic CH bonds. The vibration band phenolic C-O elongation was observed around 1337 cm⁻¹ in the free ligand in the complex, this band appears at a lower frequency to 1167 cm⁻¹ in the spectra of Fe(III) complex and at 1121 in the spectra of Cu(II) complex confirming the participation of the phenolic group in the complex formation. An absorption band P = O is observed at 1215 cm⁻¹ in the free ligand and appears to 1218 cm⁻¹ in the iron (III) complex and 1241 cm⁻¹ in the copper (II) complex confirming the complex formation. The New bands appeared at 573 and 586 cm⁻¹ are due to the stretching frequency of (M-O) band of copper (II) and iron (III) respectively (Tableau1).

Tableau 1: IR spectral data of the Diethyl (hydroxy(phenyl)methyl)phosphonate and Fe(III);Cu(II) complex

Fonction	ν (cm ⁻¹) : L1	ν (cm ⁻¹) : L1-Fe	ν (cm ⁻¹) : L1-Cu
OH	3500-3300	3263	3447
CH ₂ Ethoxy	2980	2962	2993
CH ₃ Ethoxy	2960	2979	2974
CH Aromatique	3050-3000	3046	3054
P=O	1259	1233	1241
C-O	1337	1127	1121
M-O	-	586	573

Tableau 2: IR spectral data of the dimethyl (hydroxy(phenyl)methyl)phosphonate and Fe(III);Cu(II) complex

Fonction	ν (cm ⁻¹) : L2	ν (cm ⁻¹) : L2-Fe	ν (cm ⁻¹) : L2-Cu
OH	3500-3300	3234	3239
CH ₂ Ethoxy	2960	2910	2905
CH Aromatique	3050-3000	3050	3056
P=O	1259	1269	1260
C-O	1337	1126	1119

UV-Visible spectra

The UV-visible spectrum is recorded in the field (200-800nm) and the chloroform solvent (CHCl₃). The resulting spectrum is shown in the figure 2 and exhibits an absorption band at λ_{\max} = 360 nm in the case of iron (III) complex and λ_{\max} = 225 nm in the case of the copper complex (II) these absorption bands are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

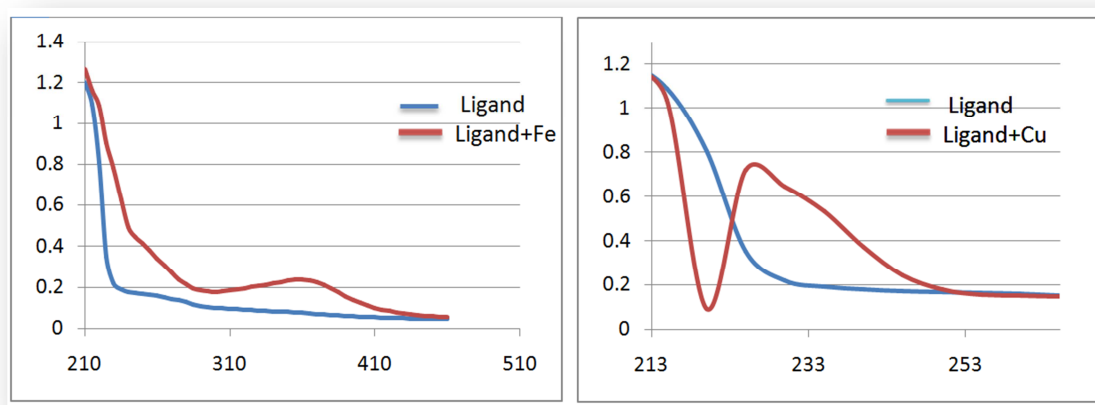
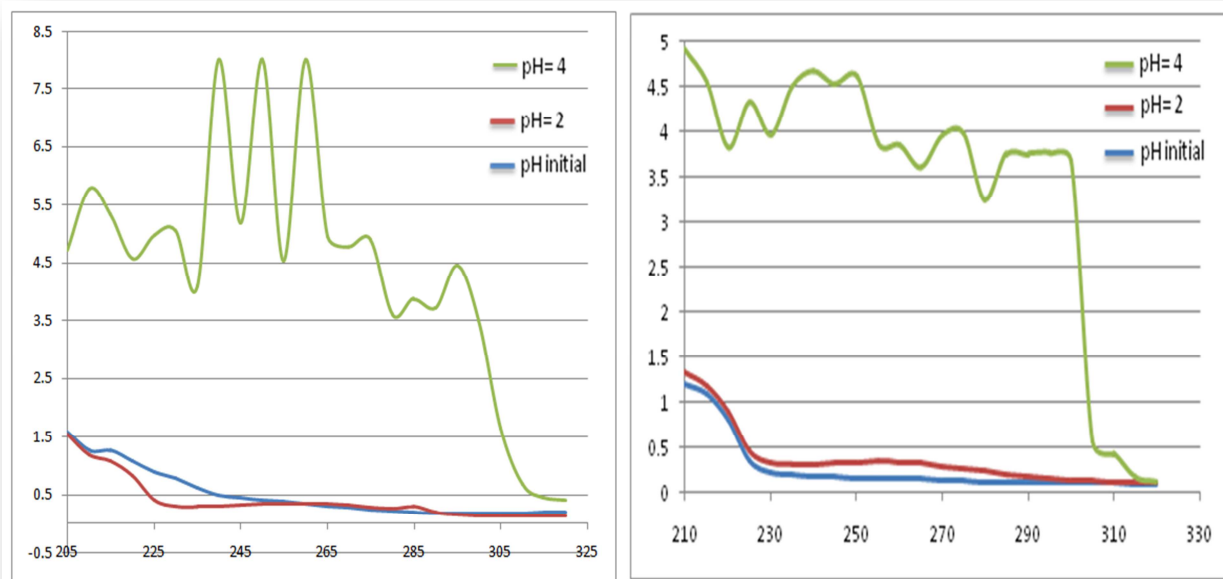


Figure 2: UV-Visible spectra of ligand and complex L-Fe, L-Cu

pH effect

The effect of pH was investigated in the range 1-5. For pH values above 5, the transitions of very low absorbance are amplified and shifted towards lower wavelengths through the normal effect of the ligand hypsochromic each ligand field. For pH values below 5 ie pH = 4 as shown by the beam spectra (Figure 3), we are in the presence of three expected bands corresponding to Fe (III) -L₁: whose very sharp maximum are 237nm, 250nm and 265 nm, the other much larger has two maxima (285 and 305nm).the result for the Cu(II)-L₁ complex shows that at pH = 4 tapes are less acute presence of three broad bands whose respective maxima are 250nm, 290nm and 270nm.

We can confirm that the absorbance increases with the pH indicating complex formation at pH = 4.



a = Fe(III)

b = Cu(II)

Figure 3: pH effects of Fe(III)-L₁ and Cu(II)-L₁ complexes

CONCLUSION

One of the most important findings of this study is the affinity of these new chelators to form highly stable complexes where practical interest in these chelating individual and phosphonates in general in the industrial treatment. The ligand phosphonate was used to coordinate iron and copper which leads to the metal complex where the ratio of (metal - ligand) was 1:2 for copper and 1:3 for iron. All the compounds of the iron(III) and the copper(II) were characterized by infra-red and UV spectroscopic.

Acknowledgements

This work was supported financially by The General Directorate for Scientific Research and Technological Development (DG-RSDT), Algerian Ministry of Scientific Research, Applied Organic Laboratory (FNR 2000).

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