

بسم الله الرحمن الرحيم





شبكة المعلومات الجامعية التوثيق الالكتروني والميكرو فيلم



جامعة عين شمس

التوثيق الإلكتروني والميكروفيلم

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لم ترد بالأصل



B12023

**STUDIES ON COMPLEXES OF GROUP IIB ELEMENTS
WITH SOME NITROGEN DONOR LIGANDS**

Thesis

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بسم الله الرحمن الرحيم

وعلمك ما لم تكن تعلم وكان فضل الله عليك عظيما

صدق الله العظيم

TO MY PARENTS,
SALSABIEL AND KARIM

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*In the name of the most merciful **GOD**, I herein enclose my deepest feelings of respect to thanks to my **Great God** for helping and guiding me throughout my career.*

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SUMMARY

This thesis comprises three chapters:

In chapter 1 a survey on metal complexes of both 2-Benzoylpyridine and picolinic acid was given and mentioned. This survey clarified several points i) complexes of both 2-benzoylpyridine and of picolinic acid have an important biological effects. ii) Only few metal complexes of 2-benzoylpyridine have been reported. iii) Although a numerous of metal-picolinic acid complexes were prepared, gold(III) halide complexes of this ligand have not yet been mentioned in the literature. iv) 2-Benzoylpyridine acts either a mono- or bi-dentate ligand in its complexes, whereas picolinic acid behaves as bidentate ligand in the most of complexes, as monodentate in few others and as tridentate one in three complexes only.

Chapter 2 is devoted for the experimental part, we isolated complexes of types $(MX)_2(2-Bzpy)$ [for $M = Cu(I)$, $X = Cl, Br$], $M(2-Bzpy)X$ [$M = Cu(I)$, $X = Cl, Br, I, SCN$ and N_3], $M(2-Bzpy)_2X_2$ [$M = Cu(II)$, $X = Br, N_3$] and $MI_2[(Ind)H]$ where $M = Cu(I)$, $Ind = 9H-indeno[2,1-b]pyridin-9-one$ (which is the oxidative and cyclized form of 2-benzoylpyridine). Different types of gold(III) complexes of both picolinic acid and 2-benzoylpyridine were also isolated.

$NaAu(pic)_2X_2 \cdot 2H_2O$ [$X = Cl, I$],

$MAuX_4 \cdot 4(pic-H) \cdot 2H_2O$ [$M = K$ for $X = Br$ and Na for $X = Cl$],

$\text{NaAuCl}_4 \cdot \text{Na}(\text{pic-H})(\text{pic}) \cdot 2\text{H}_2\text{O}$, $\text{NaAuX}_4(2\text{-Bzpy})_2$ [$\text{X} = \text{Cl}, \text{I}$], and $[\text{AuX}_4][(\text{Ind})\text{H}]$ [$\text{X} = \text{Cl}, \text{I}$]. The instruments used for the physical measurements are described.

Chapter 3 is concerned with the results and discussion of the different measurements on the isolated complexes. This chapter is divided into several parts. Part 1: This is a general section dealing with the preparation of the different types of Cu(I) complexes. Here we mentioned that the type of the isolated copper(I) complexes was found to depend on the ratio of copper to 2-benzoylpyridine and on the nature of halide or pseudohalide. When Cu/2-Bzpy ratio is 1:>1 a brown 1:1 adducts are formed, whereas the presence of excess of copper leads to yellow compounds of the formula $(\text{CuX})_2\text{L}$, where $\text{X} = \text{Cl}, \text{Br}$. In case of $\text{X} = \text{I}$ a new compound is formed which is the complex of Cu(I)I with the oxidation product of 2-benzoylpyridine. Trials to prepare corresponding compounds for $\text{X} = \text{Cl}, \text{Br}$ or N_3 led to the oxidation of Cu(I) to Cu(II) rather than the oxidation of 2-benzoylpyridine. The oxidation of 2-benzoylpyridine to 9H-indeno[2,1-b]pyridin-9-one also occurred when we used gold(III) halide to interact with 2-benzoylpyridine. The oxidation of the ligand here is dependent on the solvent rather than the halide ion. Thus, the preparation of the complexes in aqueous medium afforded complexes of gold(III) halide of 2-benzoylpyridine whereas when we

used an alcoholic medium, gold(III) halide complexes of the oxidation product were formed.

Part 2 is concerned with different types of complexes of 2-benzoylpyridine. We discuss the determination of structure of Cu(I) complexes of 2-benzoylpyridine using different physical measurements. The electronic spectra of 2-benzoylpyridine shows two bands 46,816 and 38,226 cm^{-1} in ethanol and 36,791 and 35,124 cm^{-1} in DMF which assigned as $\pi-\pi^*$ transitions. A third weak band at 29,256 cm^{-1} in ethanol and 28,490 cm^{-1} in DMF appeared and is assigned as $n-\pi^*$ transition. These two transitions appeared in the spectra of all solid complexes as a strong bands around 37,700 cm^{-1} in addition to band or shoulder around 29,400 cm^{-1} . The spectra of the brown complexes show a strong absorption band at 27,700-16,600 cm^{-1} whereas the yellow one show a strong band around 24,400 cm^{-1} . These bands are due to metal-to-ligand charge transfer band. The infrared spectra of the yellow complexes indicate that 2-benzoylpyridine is N-monodentate ligand whereas in the brown complexes the ligand is N,O-bidentate one. For the thiocyanato and azido complexes, the IR spectra show that both thiocyanate and azide ligands are bridging pseudohalide groups assuming a dimeric or polymeric structures. The far infrared of both brown or yellow copper(I) chloride adducts of 2-benzoylpyridine, suggested a bridging halide assuming a dimeric or