



Synthesis and Characterization of Some Ni(II) and Cu(II) Complexes with 2-[(4-Aminophenyl)imino]-1, 2-diphenyl-1-ethanone

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Abstract: The present work deals with synthesis and characterization of the ligand 2-[(4-aminophenyl)imino]-1,2-diphenyl-1-ethanone and their complexes with Ni(II) and Cu(II) ions. The synthesized ligand and its complexes have been characterized by elemental analysis, infrared, electronic, nuclear magnetic resonance and mass spectra. The metal ligand ratio was found to be 1:1. Square planer geometry for both complexes was suggested.

Keywords: Synthesis, Characterisation studies, Spectral, Copper coplexes.

Introduction

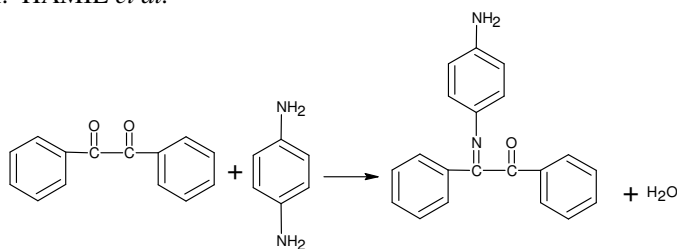
Many complexes of the type 4-dimethylaminobenzaldehyde, G-atyle-5-hexene-2-4-diones with transition metal ions have been synthesized and characterized and a square planar geometry was suggested for Ni(II) and Cr(III) and Pd(II) complexes¹. Several complexes of different ligands derived from salicylaldehyde and *o*-aminophenol or *o*-aminobenzoic acid have been synthesized and characterized using different techniques. A square planar geometry was predicted for the metal complexes². Ternary complexes of Ni(II) with 1,2-diaminopropanoecysteine, *o*-penicillamine and *L*-cysteic acid have been synthesized and characterized³.

Experimental

All chemicals used were of laboratory pure. All organic solvents were obtained as pure grade materials from BDH.

Preparation of the ligand

2-[(4-Aminophenyl)imino]-1,2-diphenyl-1-ethanone was prepared by mixing an ethanolic solution of 0.01 mol of benzil (2.0 g) with another ethanolic solution of 0.01 mol of 1,4-diaminebenzene (Scheme 1). The reaction mixture was refluxed for two hours. The formed precipitate was filtered, washed several times with ethanol and dried in a desiccator over calcium hydroxide. The yield of the reaction was 73%.



Scheme 1

Preparation of the complexes

Complexes of Ni(II) and Cu(II) ions with 2-[(4-aminophenyl)imino]-1,2-diphenyl-1-ethanone were prepared by mixing ethanolic solutions (50 mL) of 0.01 mole (3.0 g) of the synthesized ligand with an ethanolic solution (50 mL) of the 0.01 mol (2.38 and 1.71 g) of NiCl₂·6H₂O, CuCl₂·2H₂O, respectively and few drops of ammonia solution were added to adjust the pH until the complexes isolated. The reactions mixtures were refluxed for three hours and left to cool and filtered by suction. The precipitates were washed several times with chloroform, then ether. The complexes were dried in desiccators over anhydrous calcium chloride under vacuum. The yield was 73 and 78% respectively. Some physical properties of the ligand and its complexes are listed in Table 1.

Table 1. Some physical properties of the ligand and its complexes with Ni(II) and Cu(II) ions.

Ligand/ Complexes	Color	M. P °C	Solubility				
			H ₂ O	C ₂ H ₅ OH	CCl ₄	CH ₃ Cl	CH ₃ COOH
C ₂₀ H ₁₆ N ₂ O	Brown	140-142	I.S	S	I.S	I.S	I.S
[Ni(C ₂₀ H ₁₆ N ₂ O)OH]	Black	>250	I.S	S	I.S	P.S	I.S
[Cu(C ₂₀ H ₁₆ N ₂ O)OH]	Black	>250	I.S	S	I.S	P.S	I.S

S = Soluble *P.S* = Partial soluble *I.S* = Insoluble

Measurements

The ligand and its complexes with Ni(II) and Cu(II) ions were subjected to CHN elemental analyses using 2400 elemental analyzer at Micro-Analytical Center, Cairo University, Giza, Egypt. Infrared spectra were obtained by KBr disc technique by using IFS-25DPUS/IR Spectrometer (Bruker). Electronic absorption spectra were measured in nujol mull using a Perkin-Elmer-Lambda β-Spectrophotometer. The proton NMR spectra were recorded using a Varian Gemini 400 MHz Spectrometer using d⁶-DMSO solvent.

Results and Discussion

The reactions of benzil with 1, 4-diaminobenzene in ethanol yields one compound of 2-[(4-amino-phenyl)imino]-1,2-diphenyl-1-ethanone. The reaction of the prepared ligand with Ni(II) and Cu(II) metal ions leading to the formation of complexes.

Microanalysis

The elemental analyses (C, H and N) of the ligand and its complexes are listed in Table 2 and show a good agreement with the calculated values and display the formation of 1:1 [M:L] ratio.

Table 2. Elemental analysis data of the ligand and its complexes.

Complex	C%		H%		N%	
	Calc.	Found	Calc.	Found	Calc.	Found
C ₂₀ H ₁₆ N ₂ O	75.69	75.41	6.03	6.17	13.24	13.20
[Ni(C ₂₀ H ₁₆ N ₂ O)OH]	63.88	63.20	4.52	4.32	7.45	7.34
[Cu(C ₂₀ H ₁₆ N ₂ O)OH]	63.00	62.59	4.46	4.33	7.36	7.08

Infrared spectra

Infrared spectral data of the ligand (Figure 1) shows several bands at 3338, 1662 and 1606 cm^{-1} due to NH_2 , $\text{C}=\text{O}$ and $\text{C}=\text{N}$, respectively^{4,5}. The infrared spectral data of the Ni(II) and Cu(II) complexes (Figures 2 & 3) show a disappearance of the band due to the coordination of the NH_2 with the central metal ion⁶. The band at 1662 cm^{-1} which attributed to the $\text{C}=\text{O}$ in free ligand is shifted to lower frequency 1637 cm^{-1} in the spectra of the complexes. Also, the $\text{C}=\text{N}$ band in the free ligand disappeared in the spectra of the complexes due to the coordination with the central metal ion⁷. New bands at 520-500 and 700-698 cm^{-1} attributed to the existing of $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ vibrations. The appearance of these vibrations which are not present in the free ligand indicates the involvement of nitrogen and oxygen atoms in chelation⁸.

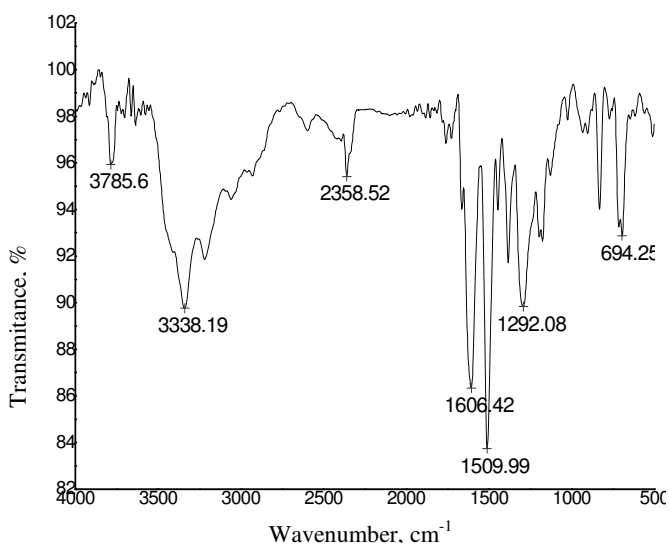


Figure 1. IR spectrum of the free ligand.

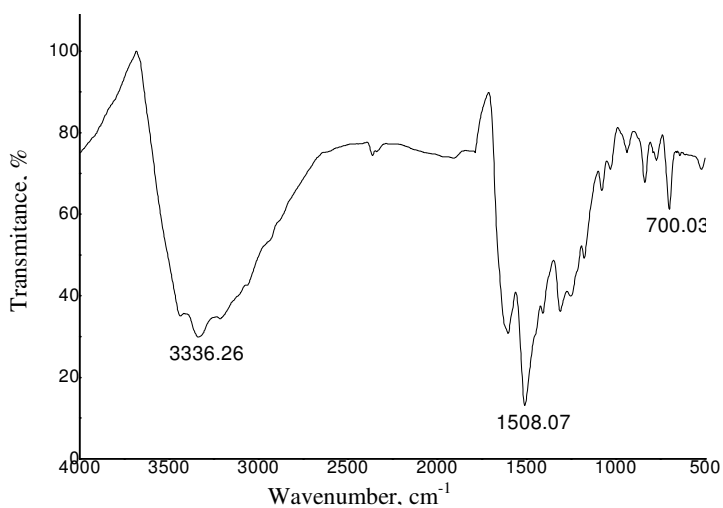


Figure 2. IR spectrum of Ni(II) complex.

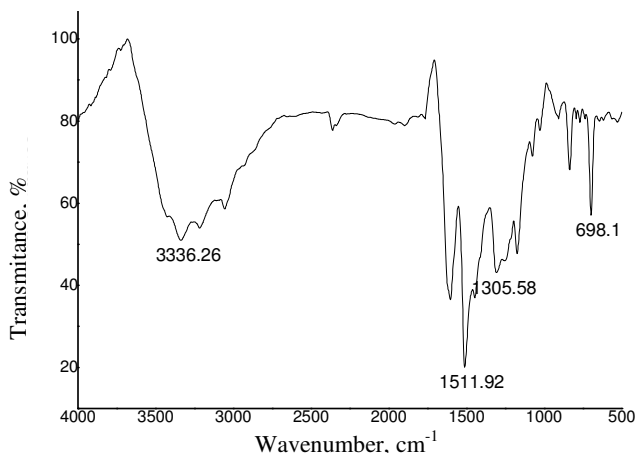


Figure 3. IR spectrum of Cu(II) complex.

Proton nuclear magnetic resonance spectrum of the ligand

¹H NMR spectral data of the ligand was recorded in d⁶-DMSO show bands at 7-8 and 3.3 ppm, assigned to phenyl protons and NH₂ group, respectively⁹.

Mass spectral fragmentation of the ligand

The mass spectrum of the ligand (Figure 4) exhibits some peaks illustrates the proper fragmentations, the peak at $m/e^+ = 300$ are corresponding to the original ligand, while the peak at $m/e^+ = 195$ is due to the lose of C₆H₅-C=N- C₆H₅-NH₂ and the peak at $m/e^+ = 92$ is attributed to the presence of -C₆H₅.

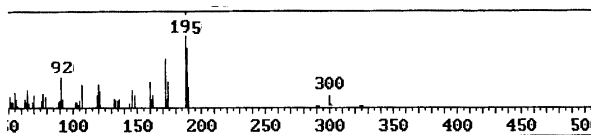


Figure 4. Mass spectrum of the ligand.

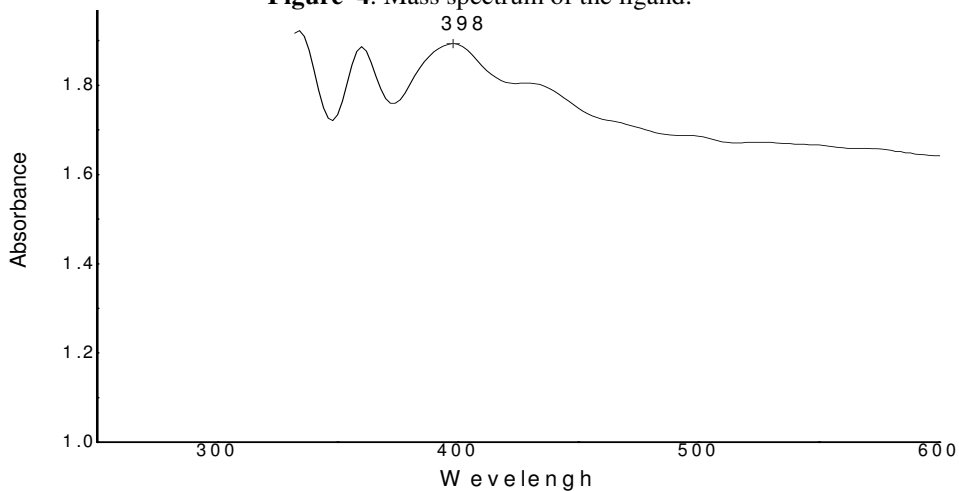


Figure 5. Ultraviolet spectrum of the ligand.

Electronic spectra

The electronic absorption spectra of the ligand (Figure 5) display two bands at 360 and 398 nm which are due to $\pi \rightarrow \pi^*$ (phenyl ring) and $n \rightarrow \pi^*$ ($-\text{C}=\text{N}$), respectively. The electronic spectra of Ni(II) and Cu(II) complexes (Figures 6 & 7) show three bands each at 398, 465, 560 nm and 398, 530, 640 nm, respectively which could be due to d-d and charge transfer transitions. A square planar geometry was suggested for both complexes¹⁰.

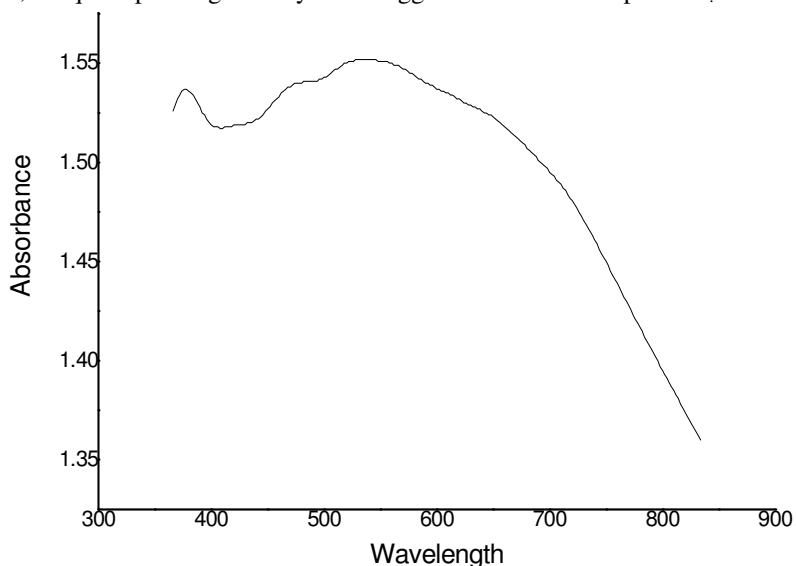


Figure 6. Electronic spectrum of Ni(II) complex.

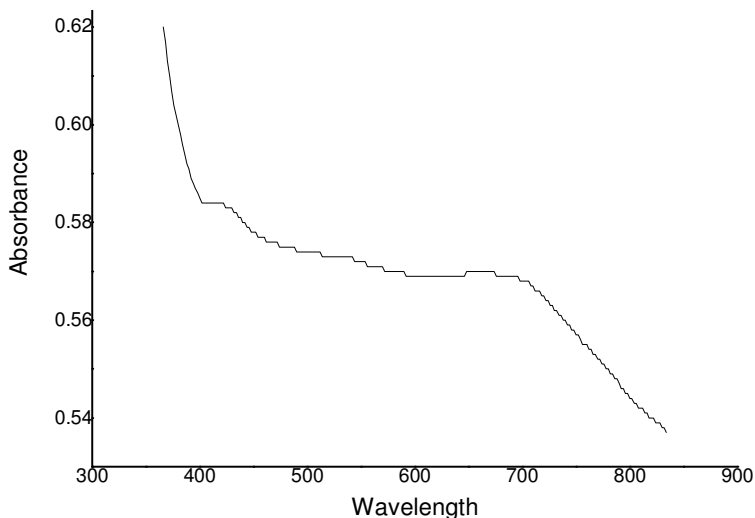
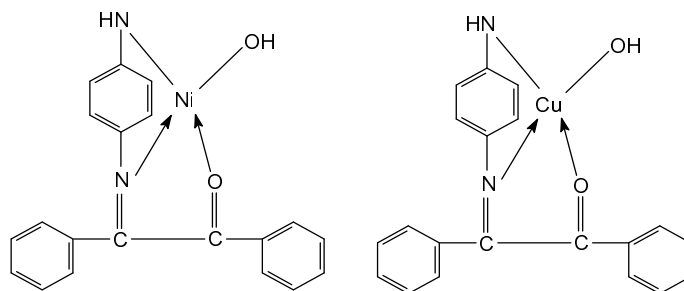


Figure 7. Electronic spectrum of Cu(II) complex.

Conclusion

Form the previous analyses, we can conclude that the complexes have a square planar structure in which the ligand coordinated to the metal ion as a tridentate *via* two nitrogen and one oxygen atom. The suggested geometrical structures (Scheme 2) are shown below:



Scheme 2.

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