http://www.e-journals.net

ISSN: 0973-4945; CODEN ECJHAO
E-Journal of Chemistry
2010, **7(1),** 49-54

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

K.M.KHALIFA, A.M.HAMIL*, A.GASEM and A.ABDULSALAM

Chemistry Department, Faculty of Science,
Sebha University, Sebha, Libya.
abdsalam_1956@maktoob.com

Received 28 March 2009; Accepted 14 May 2009

Abstract: The present work deals with synthesis and characterization of the ligand 2-[(4-aminophnyl)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

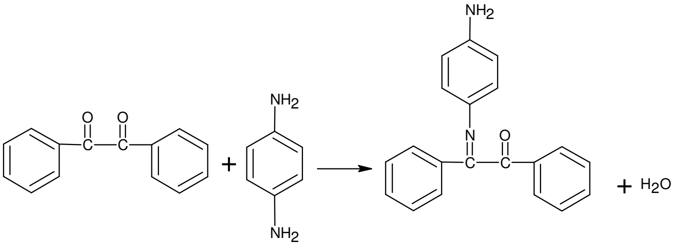
Many complexes of the type 4-dimethylaminobenzaldehyde, G-atyle-5-hexene-2-4-diones with transition metal ions have been synthesized and characterized and a square planar geometry was suggested for Ni(II) and Cr(III) and Pd(II) complexes[1]. Several complexes of different ligands derived form salicylaldehyde and *o*-aminophenol or *o*-aminobenzoic acid have been synthesized and characterized using different techniques. A square planar geometry was predicted for the metal complexes[2]. Ternary complexes of Ni(II) with 1,2-diaminopropanoecysteine, *o*-penicillamine and *L*-cysteic acid have been synthesized and characterized[3].

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-Aminophnyl)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 $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, 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}C	Solubility				
			H_2O	C_2H_5OH	CCl_4	CH_3Cl	CH_3COOH
$C_{20}H_{16}N_2O$	Brown	140-142	I.S	S	I.S	I.S	I.S
$[Ni(C_{20}H_{16}N_2O)OH]$	Black	>250	I.S	S	I.S	P.S	I.S
$[Cu(C_{20}H_{16}N_2O)OH]$	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-Spetrophotometer. The proton NMR spectra were recorded using a Varian Gemini 400 MHz Spectrometer using d^6-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
$C_{20}H_{16}N_2O$	75.69	75.41	6.03	6.17	13.24	13.20
$[Ni(C_{20}H_{16}N_2O)OH]$	63.88	63.20	4.52	4.32	7.45	7.34
$[Cu(C_{20}H_{16}N_2O)OH]$	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$_2$, C=O and C=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 ion[6]. The band at 1662 cm^{-1} which attributed to the C=O in free ligand is shifted to lower frequency 1637 cm^{-1} in the spectra of the complexes. Also, the C=N band in the free ligand disappeared in the spectra of the complexes due to the coordination with the central metal ion[7]. New bands at 520-500 and 700-698 cm^{-1} attributed to the existing of υ(M-N) and υ(M-O) vibrations. The appearance of these vibrations which are not present in the free ligand indicates the involvement of nitrogen and oxygen atoms in chelation[8].

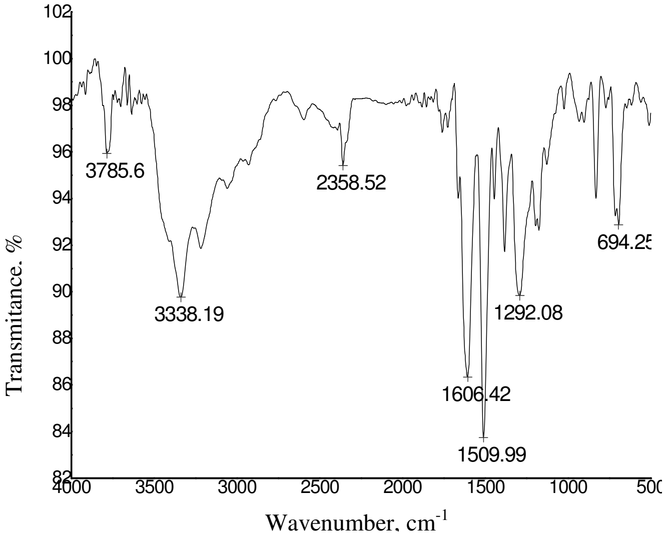


Figure 1. IR spectrum of the free ligand.

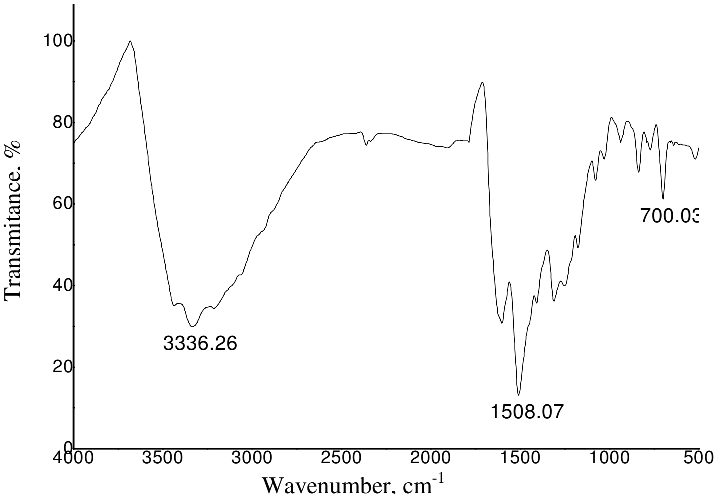


Figure 2. IR spectrum of Ni(II) complex.

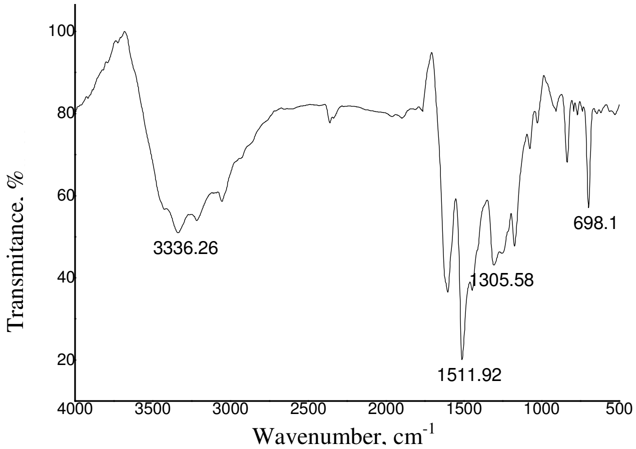


Figure 3. IR spectrum of Cu(II) complex.

Proton nuclear magnetic resonance spectrum of the ligand

${}^1H$ NMR spectral data of the ligand was recorded in d^6-DMSO show bands at 7-8 and 3.3 ppm, assigned to phenyl protons and NH_2 group, respectively[9].

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 C_6H_5-C=N- C_6H_5-NH_2 and the peak at *m/e*$^+$ = 92 is attributed to the presence of –C-C_6H_5.

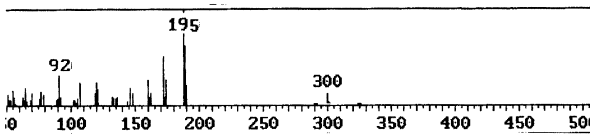


Figure 4. Mass spectrum of the ligand.

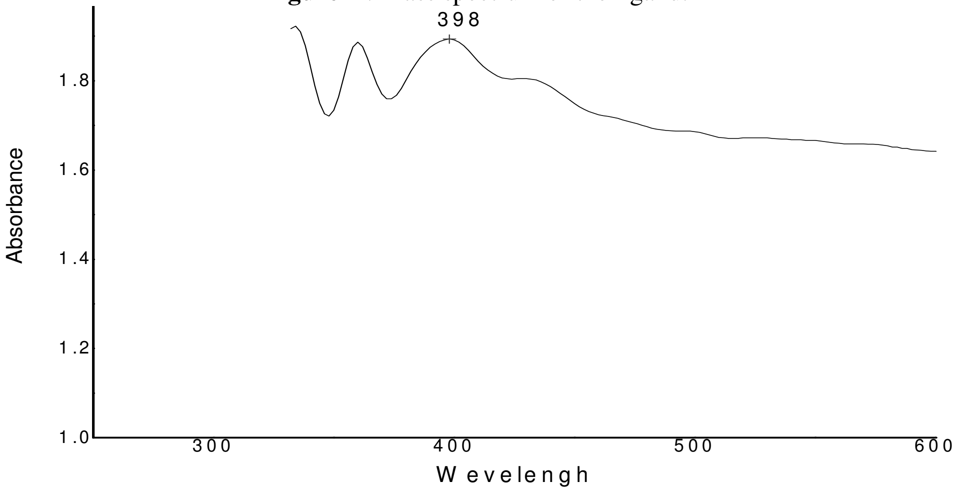


Figure 5. Ultraviolet spectrum of the ligand.

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 $n \rightarrow \pi^*$ (-C=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 were suggested for both complexes[10].

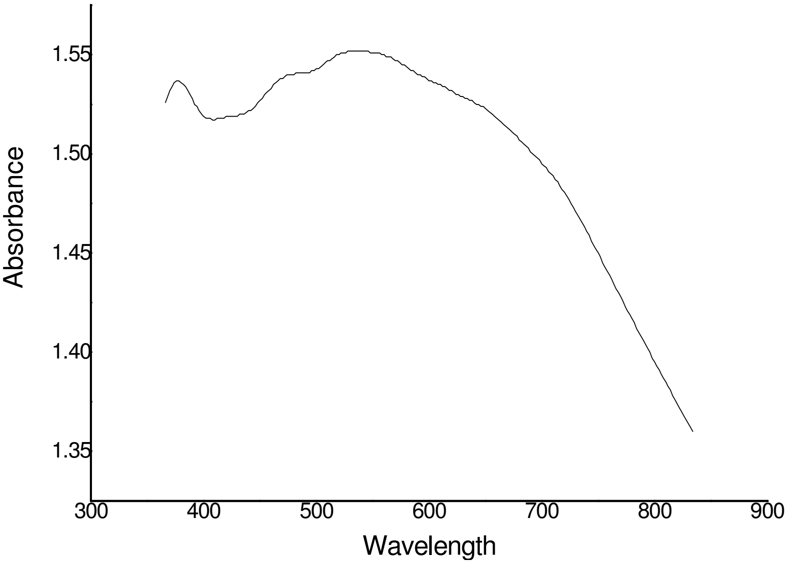


Figure 6. Electronic spectrum of Ni(II) complex.

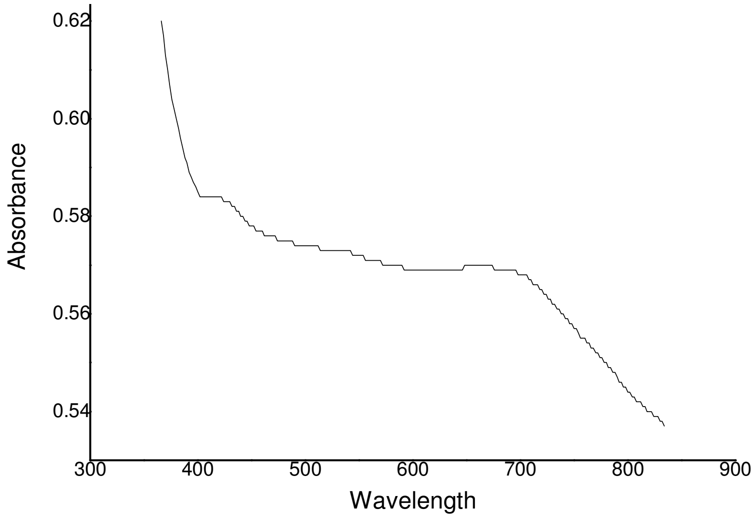
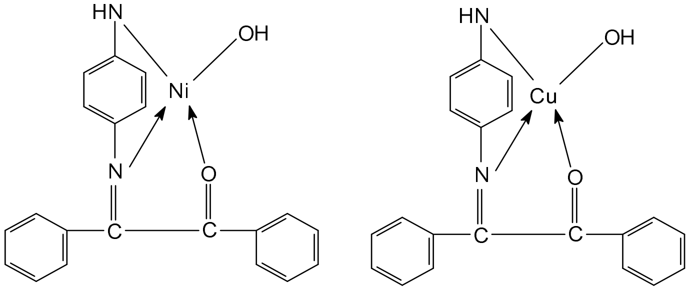


Figure 7. Electronic spectrum of Cu(II) complex.

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.

References

1. Nakai R, Sugai M and Nakaao H, *Pharm Bull.*, (Tokyo), 1957, **5**, 576.
2. Ben-Saber S M, Maihub A A, Hudere S S and El-ajaily M M, *Microchemical J*, 2005, **81**,191-194.
3. Curtius T, *J Prakt Chem.*, 1894, **52**, 278.
4. Pitt C G and Fowler, *J Am Chem Soc.*, 1967, **89**, 6794.
5. M.El-Roudi, *Bull Fac Sci.*, *Assiut University*, 1989, **18**, 7-12.
6. Bellamy J, Infrared spectra of organic molecules, 1st Ed., Wiley, London, 1975.
7. El-zwaey R S, El-ajaily M M and Maihub A A, *Asian J Chem.*, 2009, **21(1),** 31-35.
8. Jezowska B, Lisowski J and Chemielewski P, *Polyhedron*, 1988, 7(5), 337-340.
9. El-ajaily M M, Maihub A A, Abuzida M A, Aboukrish M M, Amer A A and Asaih E A, *Asian J Chem.*, 2007, **19(1),**781-783.
10. El-ajaily M M and Maihub A A, *Jerash for Research and Studies*, 2003, **8(1),** 5-12.