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Pelagia Research Library

Der Chemica Sinica, 2013, 4(5):62-66

Pelagia Research Library

ISSN: 0976-8505
CODEN (USA) CSHIA5

Synthesis, characterization and antimicrobial studies on nickel (II) and copper (II) complexes of $2N_2O_2$ donor schiff base

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ABSTRACT

The ligand and its complexes of Ni(II) and Cu(II) were investigated in terms of synthesis, elemental analysis, infrared; electronic spectra, thermal analysis and antibacterial and antifungal activities. The results shows that the complexes are formed with 2M:L (2Metal:1ligand) molar ratio. Tetradentate Schiff base ligand with $2N_2O_2$ donor atoms is coordinated to Ni(II) and Cu(II) ions to form the corresponding complex. Antibacterial and antifungal activity of the synthesized ligand and its complexes was tested against selected pathogenic bacteria and fungi. Cu_2L complex showed more antifungal activity than (Ni_2L) analogous. The complexes are possessed microorganism activities higher than that of the free ligand.

Keywords: Synthesis and antimicrobial, 3,3'-diaminobenzidine and salicylaldehyde.

INTRODUCTION

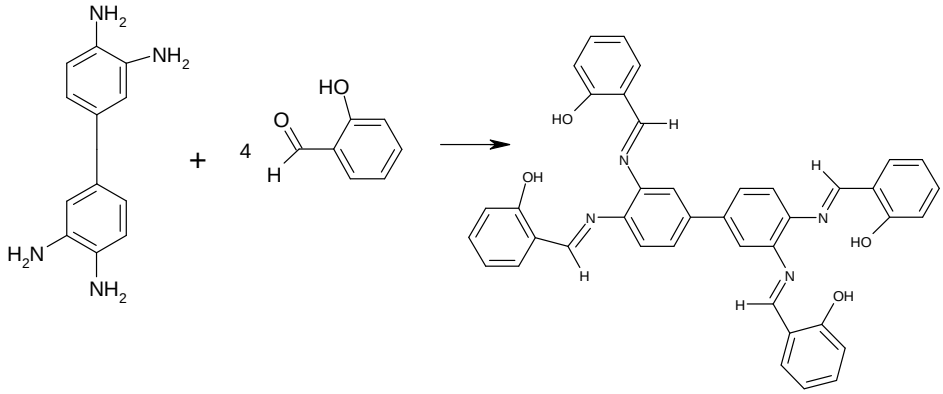
Schiff bases have been widely used as ligands because of high stability of the coordination compounds and their good solubility in common solvents. The π-system in a Schiff base often imposes a geometrical constriction and affects the electronic structure as well. Thermo chemical properties of Schiff bases have attracted much researcher attention in view of their ability to coordinate metal ions, acting as bidentate or tetradentate ligands in metal chelates involving a NO or N_2O_2-Schiff-base donor atom sets. The complexes with salen ligands derived from the condensation of salicylaldhyde with diamine are widely studied. [1-4]. The mechanism of imine formation begins as nucleophilic addition to the carbonyl group, in this case the nucleophilic is the amine which reacts with the aldehyde or ketone to give an imines [5]. Octahedral complexes of Ni(II) are obtained especially with neutral N-donor ligands and the O-donor. The four-coordinate complexes of Ni(II), those with the square planar stereochemistry are the most numerous. They include the yellow $[Ni(CN)_4]^2$, the red bis(N-methylsalicylaldiminato)nickel(II) and well-known bis(dimethylglyoximato) nickel(II). Although less numerous than the square planar complexes, tetrahedral complexes of Ni(II) also occur [6-7]. Cu(II) is the most effective available divalent ion for bending to organic molecule [8-9]. In the octahedral arrangement of Cu(II) the Jan-Teller effect arising from the unequal occupation of the e_g pair of orbitals (d_z^2 and $d_{x^2-y^2}$) when a d^9 ion is subjected to an octahedral crystal field. Copper(II) also forms stable complexes with O-donor ligands. Mixed O, N-donor ligands such as Schiff bases are of interest in that they provide example square planar coordination [6]. Ni(II) and Cu(II) complexes of the Schiff base derived from vanillin and DL-α-aminobutyric acid were found to exhibit higher antibacterial activity compared to the free Schiff base [10].

MATERIALS AND METHODS

All materials and reagents used in this study were laboratory pure chemicals. They include 3,3'-diaminobenzidine and salicylaldehyde. The solvents and metal salts are used as they received from the supplier without further purification. The synthesis of Schiff-base ligand and its complexes are based on the methods reported previously [11].

Synthesis of the Schiff base ligand

3,3'-diaminobenzidine (1moles) was stirred with salicylaldehyde (4 moles) in 100 cm^3 dry ethanol for 1h. A yellow solid crude product is filtered off, wash several times with small portions of ethanol and finally with diethyl ether. Orange plate-shaped obtained and dried in desiccated over silica gel.



Synthesis of Ni(II) Complex

The ligand (1 mole) was dissolved in (100 cm^3) absolute methanol and added to another methanolic solution (50 cm^3) of Nickel acetate $Ni(C_2H_3O_2)_2.4H_2O$ (2 mol).The mixture was stirred at room temperature for one day. The red precipitate product is collected by filtration and washed several times with methanol and dried in desiccated over silica gel.

Synthesis of Cu(II) Complex

The ligand (1 mole) was dissolved in (100 cm^3) absolute methanol and added to another methanolic solution (50 cm^3) of Cupric chloride $CuCl_2.2H_2O$ (2 mol).The mixture was stirred at room temperature for one day. The brown precipitate product is collected by filtration and washed several times with methanol and dried in desiccated over silica gel.

Measurements

The Schiff base ligand and its complexes under investigation were subjected to (C, H and N) elemental analysis which performed using 2400 elemental analyzer at the Micro-Analytical Center, Faculty of Science, Assiut University, Assiut, Egypt. The differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the Schiff base complexes were carried out using shimadzu DTH-60H thermal analysis at thermal analysis unit of central laboratory of Assiut University (Egypt). The melting point of ligand and its complexes were measured in capillary tubes Philip Haris, Shenston-England serial NO.B/A-211, at Chemistry Department. Faculty of Science, University of Benghazi. The IR spectra of the Schiff base ligand and its complexes were recorded as KBr discs on a Shimadzu IR400-91527, at the Faculty of Pharmacy, Assiut University, Assiut, Egypt. The electronic spectra of the Schiff base ligand and its complexes were measured by the applying dimethylformamide (DMF) as solvent using UV-Vis-NIR 3101pc Shimadzu at Chemistry Department, Faculty of Science University of Benghazi. The strains of bacteria and fungi were used are Escherichia coli, Staphylococcus aureus , Staphylococcus epidermidis , Micrococcus spp. , Pseudomonas Aeruginos, Klebsiella pneumonia, Salmonella typhimurium, Aspragillus niger and Candida albicans. They were grown overnight at 37°C in Mueller-Hinton Broth at pH 7.4 [12-13], this study was done in faculty of pharmacy, microbiology Department, Zagazig university, Egypt. Yeast and mould extract agar was used for testing antifungal activity and the above method as for bacteria were adopted [14]. Sensitivity test of the ligand and its complexes on the bacteria and fungi were compared with sensitivity to common antibiotics

(Cefotaxime, Amoxicillin, Nystatin and Amphotericin B). The antibiotics were placed on the surface of the culture medium which contains the same bacteria and fungi used in this study.

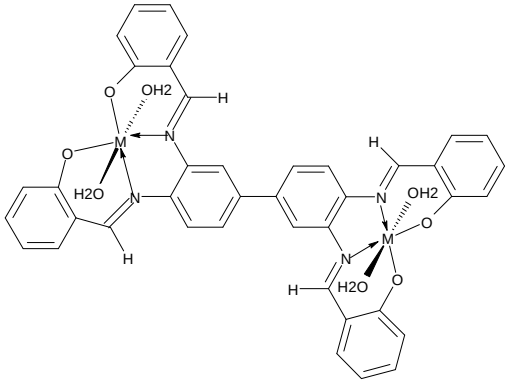
RESULTS AND DISCUSSION

Elemental analysis

The elemental analysis of C, H and N of the complexes are listed in Table 1. The results of C, H and N percentage are in accord with the composition suggested for the ligand and the complexes.

Table 1: Elemental analysis and some physical properties of the ligand and its complexes

Compound	Formula Weight	M.P./ ºC	Microanalysis (Calc.)		
			%C	%H	%N
H_4L	630	240	76.18 (75.25)	4.79 (4.76)	8.88 (8.40)
$[Cu_2L.4H_2O]\ H_2O$	753.09	294	56.93 (56.55)	4.27 (4.95)	6.64 (7.82)
$[Ni_2L.4H_2O]$	743.38	300	58.86 (58.35)	4.16 (4.49)	6.86 (6.65)



The complex structures (M= Ni or Cu)

Thermal analysis

The ligand reveals three endothermic peaks and two exothermic ones. The endothermic peak at 40 ºC which is due to broken of hydrogen bonding, another endothermic peak appears at 90 ºC may due to phase transformation. Endothermic peak observed at 231 ºC, assigned to melting point. Exothermic peaks appeared at 255, 295, 345, 365 and 385 ºC with weight loss 59.3 % (Calc. 59.4 %), corresponding to loss of 4 C_6H_5O group. The final exothermic peak observed at 435 ºC with weight loss of 37.91 % (Calc. 37.21 %) may be due to loss of 2 CO_2. Cu_2(L) complex shows broad endothermic peak at 45 – 130 ºC, may be due to loss of one hydrated water molecule with weight loss 2.12 % (Calc. 2.13 %) and loss of four coordinated water molecules with weight loss 8.33 % (Calc. 8.72 %). Another endothermic peak appeared at 360 ºC, may be due to melting point of the complex. Exothermic peaks observed at 240, 350, 400 and 440 ºC with weight loss 50.0 % (Calc. 49.34 %) is corresponding to loss of 4 C_6H_5O groups. Oxidative thermal decomposition occurs at 490 ºC with endothermic peak leaving 2 CuO with weight loss 41.67 % (Calc. 41.88 %).

Table (2): Thermal analysis of copper complex

complexes	Water of hydration weight loss %	No. of water molec.	Water of Coord. weigh loss	No. of water coord.	$4C_6H_5O$ groups weight loss	Temp. ºC	M O weight loss	Temp. ºC
$[Cu_2L.4H_2O]$ H_2O	(2.12) (2.13)	1	(8.33) (8.72)	4	(50.0) (49.34)	240-440	(41.67) (41.88)	490

The infrared study

The important infrared stretching frequencies of the prepared Schiff base complexes are given in Table (3).The IR spectra of the complexes are compared with that of the free ligand to determine the changes that might have taken place during the complexation. The band at 1603 cm^{-1} is characteristic of the azomethine presents in the free ligand.

The lowering in this frequency region (1595–1590 cm^{-1}), observed in the two complexes, indicates the involvement of the azomethine in the coordination to the metal(II) ion [15-16]. The complexation process takes place through two nitrogen atoms of the imine groups and the two hydroxyl group of the salicylaldehyde, i.e., the ligand is tetradentate. Abroad bands in the range 3510 – 3220 and 3250 - 3020 cm^{-1} confirms the presence of water molecules [17]. Characteristic absorption bands for (M-N) and (M-O) of the complexes appear respectively in the region of 545 - 510 cm^{-1} and 590 - 554 $cm.^{-1}$ The C-OH stretching modes of the ligand appears at 1265 cm^{-1}, these bands shift to lower wave numbers as a result of coordination through the hydroxyl oxygen atoms.

Table (3) Infrared band assignments (cm^{-1}) of the ligand and its complexes

Compound	*ν*(OH) / H_2O / H- bond	*ν*(C=N)	*ν*(C-OH) / *ν*(C-O)	*ν*(M-N)	*ν*(M-O)	*ν*(Ar)
H_4L	3460 3520 – 2980 2970 - 2350	1603	1265	–	–	1556, 820 1545, 720
$[Ni_2L.4H_2O]$	3470 – 3260 3250 – 3150	1590	1180	545	590	1550, 802 1540, 750
$[Cu_2L.4H_2O]$ H_2O	3510 – 3260 3250 - 3020	1595	1182	510	554	1550, 800 1540, 752

The electronic spectra

The electronic spectra of Schiff base complexes are performed in DMF solvent and the band assignment are shown in Table (4). The octahedral Cu(II) complex exhibited only a single band due to the transition $^2Eg \rightarrow {}^2T_2g$ (D), an absorption band at (21739 cm^{-1}) is assigned to a slightly distorted octahedral geometry for the complex [18]. The electronic spectrum of the Ni (II) complex displays two bands (assigned as V_2 and V_3 absorption bands respectively), (18050 cm^{-1} and 14367 cm^{-1}), assignable to $^3A_2g \rightarrow {}^3T1g$ (F) and $^3A_2g \rightarrow {}^3T_1g(P)$ transitions, respectively which are clearly indicates that the complex has six coordination octahedral geometry [19].

Table (4): Electronic spectral data (nm, cm^{-1}) of the complexes

ligand / complexes	λ_{max} Nm	cm^{-1}
$[Cu_2L.4H_2O]$ H_2O	460	21739
$[Ni_2L.4H_2O]$	554, 696	18050, 14367

Table 5: Microbiological activity against the Gram-positive bacteria and Gram-negative bacteria

Sample	Diameter (mm) of inhibition zones against the corresponding standard microorganisms						
	Gram-positive bacteria			Gram-negative bacteria			
	Staphylococcus aureus ATCC 6538	*Staphylococcus epidermidis* ATCC 12228	Micrococcus *spp.* ATCC 10240	*Pseudomonas aeruginosa* ATCC 9027	*Klebsiella pneumonia* ATCC 27736	*salmonella typhimurium* ATCC 14028	*Escherichia coli* ATCC 10536
Ligand	17	16	16	20	21	17	19
Ni_2L	14	14	16	20	21	16	18
Cu_2L	20	19	20	21	22	19	20
Cefotaxime (control)	34	33	43	30	37	36	35
Amoxicillin (control)	35	34	40	-	-	29	30
Nystatin (control)	-	-	-	-	-	-	-
Amphotericin B(control)	-	-	-	-	-	-	-
DMF (control)	-	-	-	-	-	-	-

The antimicrobial activities

The antimicrobial activity for the free ligand and the complexes are represented in Table (5,6). It shows the inhibition zones of bacteria and fungi growth of the Schiff base and its complexes Ni(II) and Cu(II) against *Escherichia coli. Staphylococcus aureus*, *Staphylococcus epidermidis*, *Micrococcus spp.*, *Pseudomonas Aeruginos, Klebsiella pneumonia, Salmonella typhimurium, Aspragillus niger, Candida albicans.acidophilus*. The (Cu_2L) complex shows the maximum antimicrobial activity against *Micrococcus spp.* Also the sample (Cu_2L) showed the

more antifungal activity than (Ni_2L) sample. The sample (Cu_2L) has more antifungal activity than antibacterial activity, and microorganism activity of the complexes is higher than that of the free ligand

Table 6: Microbiological activity against the Fungi

Sample	Diameter (mm) of inhibition zones against the corresponding standard microorganisms	
	Fungi	
	Aspragillus niger ATCC 16404	*Candida albicans* ATCC 10231
Ligand	15	20
Ni_2L	13	20
Cu_2L	24	20
Cefotaxime(control)	-	-
Amoxicillin(control)	-	-
Nystatin(control)	25	20
Amphotericin B(control)	16	22
DMF (control)	-	-

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