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BINUCLEAR Cu(II) COMPLEXES OF ONO TRIDENTATE HETEROCYCLIC SCHIFF BASE DERIVED FROM N-AMINOPYRIMIDINE WITH SUBSTITUTES SALICYLALDEHYDE OR 2-HYDROXYNAPHTHTALDEHYDE

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ABSTRACT

New binuclear Cu(II) complexes of ONO tridentate heterocyclic Schiff base derived from 1-amino-5-benzoyl-4-phenyl-1H pyrimidine-2-one with substitutes salicylaldehyde and 2-hydroxynaphthaldehyde have been synthesized and characterized on the basis of elemental analyses, UV, IR spectra, and also by aid of molar conductivity measurements, magnetic moment measurements. It has been found that the Schiff bases with Cu(II) ion forming binuclear complexes on 1:1 (metal:ligand) stoichiometry. Distorted octahedral environment is suggested for metal complexes. All the complexes are non electrolyte by the conductivity data

Keywords: Binuclear complexes; Substitutes salicylaldehyde; N-amino pyrimidine.

2-HİDROKSİ NAFTALDEHİD VE SÜBSTİTUE SALİSİLALDEHİTLER İLE N-AMİNOPİRİMİDİNDEN TÜREYEN BİNÜKLEER Cu(II) KOMPLEKSLERİ

ÖZET

1-Amino-5-benzoyl-4-phenyl-1H pyrimidine-2-one ile substitute salisilaldehid ve 2-hidroksinaftaldehit'den türeyen ONO üç dişli heterosiklik Shiff bazlarının yeni binükleer Cu(II) kompleksleri sentezlendi ve elemental analiz, IR, UV, magnetic moment ve molar iletkenlik ölçümleriyle karakterize edildi. Bu Schiff bazlarının Cu(II) metal iyonuyla 1:1 metal/ligand oranında binükleer kompleks oluşturdukları bulunmuştur. Bütün komplekslerin bozunmuş oktahedral yapıda oldukları düşünülmektedir. İletkenlik verilerine göre tüm kompleksler elektrolit değildirler.

Anahtar kelimeler: Binükleer kompleksler ; Substitue salisilaldehid ; N-amino pirimidine

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1. INTRODUCTION

Amino heterocycles containing two or more potential donor centers play an important role in the study of competitive reactivity of ambidentate ligand systems [1]. Heterocyclic diazines, such as pyridazine and pyrimidine, are known to act as bidentate or tridentate ligands when coordinated to metal ions [2]. Diazine ligands such as pyrimidine can form mononuclear and binuclear complexes [3-6]. Transition metal complexes containing an pyrimidine ligand are commonly found in biological media and play important roles in processes such as catalysis of drug interaction with biomolecules [7]. N-Aminopyrimidine Schiff base chemistry is less extensive and our laboratory has been exploring this chemistry [8-12]. This paper describes the synthesis of the binuclear Cu(II) complexes of some heterocyclic Schiff base ligands (Figure 1.) containing a ring of the pyrimidine. Spectral and magnetic studies have been used to characterize the structure of the complexes.

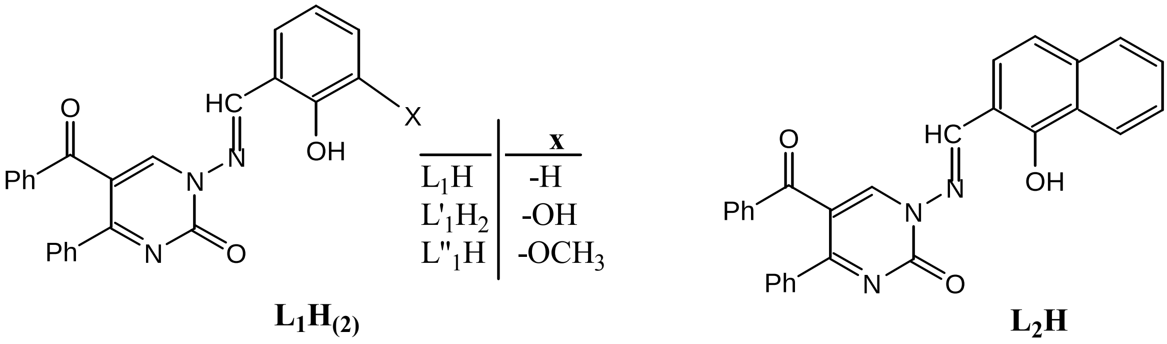


Figure 1. Stucture of the N-amino pyrimidine Schiff base ligands.

2. EXPERIMENTAL

All the chemicals and solvents used for the synthesis were reagent grade. Salicylaldehyde, 3-hydroxysalicylaldehyde, 3-methoxysalicylaldehyde and 2-hydroxy-naphthaldeyde were obtained from Fluka and Aldrich. The metal salt $Cu(AcO)_2.H_2O$ was obtained from E. Merck. All solvents were dried and purified before used. 1-Amino-5-benzoyl-4-phenyl-1H pyrimidine-2-one was prepared as described previously [13]. Elemental analyses (C, H, N) were performed by using a Carlo Erba 1106 elemental analyzer. The IR spectra were obtained using KBr discs (4000-400) cm^{-1} on a Bio-Rad-Win-IR spectrophotometer. The electronic spectra in the 200-900 nm range were obtained in DMF on a Unicam UV2-100 UV/Visible spectrophotometer. TG measurements were carried out by a Shimadzu-50 thermal analyzer. Magnetic measurements were carried out at room temperature by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant. Molar conductance of the Schiff base ligand and their transition metal complexes were determined in DMF at room temperature by using a Jenway model 4070 conductivity meter.

2.1. Preparation of the Schiff base ligands

All the ligands were prepared by condensation of 1-amino-5-benzoyl-4-phenyl-1H pyrimidine-2-one with salicylaldehyde [8], 3-hydroxysalicylaldehyde [9], 3-methoxysalicyl-aldehyde [10] and 2-hydroxynaphthaldehyde [11] in n-BuOH or EtOH. This preparation was performed as cited in the literature.

2.2 Preparation of the binuclear metal complexes

1.00 mmol of the ligands were dissolved in 30 ml of chloroform, and a solution of 1.00 mmol of the metal salt [$Cu(AcO)_2.H_2O$ (0.20 g),] in 15 ml methanol was added dropwise with continuous stirring. The mixture was stirred further for 1.5-2.5 h. at 80 ^oC. The precipitated solid was then filtered off, washed with diethylether, followed by cold ethanol and dried in vacuum desiccators. The same method was applied for the preparation of all other Cu (II) complexes by using the corresponding 5-benzoyl-1-[(2-hydroxy-benzylidene)-amino]-4-phenyl-1*H*-pyrimidin-2-one, 5-benzoyl-1-[(2,3-dihydroxy-benzylidene)-amino]-4-phenyl-1*H*-pyrimidin-2-one, 5-benzoyl-1-[(2-hydroxy-3-methoxy-benzylidene)-amino]-4-phenyl-1*H*-pyrimidin-2-one or 5-benzoyl-1-[(1-hydroxy-naphthalen-2ylmethylene)-amino]-4-phenyl-1*H*-pyrimidin-2-one working in the same conditions with their respective molar ratio.

3. RESULT AND DISCUSSION

The Schiff bases ligands are soluble in common organic solvents. But, its metal complexes are generally soluble in DMF and DMSO. The elemental analytical data of the complexes reveal that the compounds have a metal:ligand anion stoichiometry of 1:1. The analytical data and other spectral analysis are in good agreement with the proposed stoichiometry of the complexes. The colors, yields, melting points, IR and electronic absorption spectral data of all the compounds are presented in Table 1. The molar conductances of the solutions of the all the complexes in DMF are in the range 1.1-5.5 Ω^{-1} cm^2 $mole^{-1}$ (Table 1). These observations suggest that all the complexes are non-electrolytes [14] in DMF (1.10^{-3} M) at room temperature.

Polydentate complexes were obtained from 1:1 molar ratio reactions with metal ions and LH or LH_2 ligands. The ligands L_1H, L'_1H_2, L''_1H and L_2H on reaction with $Cu(CH_3COO)_2{\cdot}H_2O$ salt yields complexes corresponding to the formulas $[Cu_2(L_1)_2(Ac)_2(H_2O)_2]{\cdot}4H_2O$, $[Cu_2(L'_1)_2]{\cdot}H_2O$, $[Cu_2(L''_1)_2(Ac)_2(H_2O)_2]$, $[Cu_2(L_2)_2(Ac)_2]$.

The metal-to-ligand ratio of the Cu(II) binuclear complexes was found to be1:1 in addition to the two acetate ligands and L_1H and L''_1H complexes have additional water coordinated molecules.

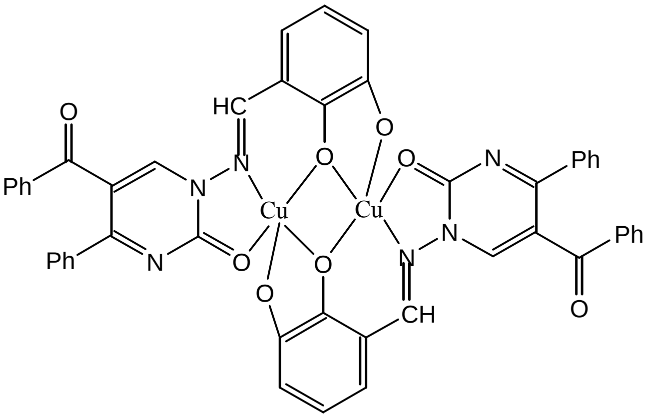
Table 1.

Analytical and physical data of all the compounds

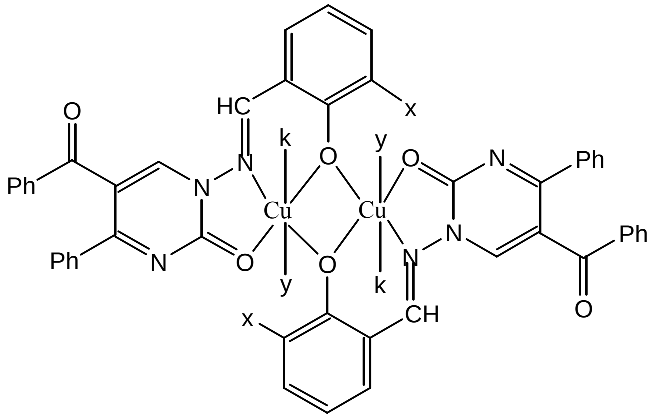
Compounds	Yield	μ_{eff}	M.p	Elemental Analyses Calculated (Found) %			
	%	[B.M]	(°C)	C	H	N	Λ_M (S cm^2 mol^{-1})
$[Cu_2(L_1)_2(Ac)_2(H_2O)_2]\cdot 4H_2O$ $C_{52}H_{50}N_6O_{16}Cu_2$ (Brown)	73.0	1.16	225	54.6 (54.3)	4.3 (4.0)	7.3 (7.1)	3.1
$[Cu_2(L'_1)_2]\cdot H_2O$ $C_{48}H_{32}N_6O_9Cu_2$ (Brown)	66.0	1.01	232	59.8 (59.8)	3.2 (3.4)	8.7 (8.3)	5.3
$[Cu_2(L''_1)_2(Ac)_2(H_2O)_2]$ $C_{54}H_{46}N_6O_{14}Cu_2$ (Brown)	76.0	0.7	180	57.4 (57.2)	4.1 (4.3)	7.4 (7.7)	5.5
$[Cu_2(L_2)_2(Ac)_2]$ $C_{56}H_{42}N_6O_{10}Cu_2$ (Brown)	65.0	0.95	243	63.5 (63.1)	3.7 (3.5)	7.4 (7.8)	1.1

3.1 Infrared spectral study

The most important infrared spectral bands of the investigated metal complexes in the present article are summarized in Table 2. The free Schiff base ligands are characterized by strong bands at 1691-1645, 1625 and 1273 cm^{-1} for L_1H, 1691-1646, 1622 and 1273 cm^{-1} for L'_1H_2, 1720-1651, 1625, 1293 cm^{-1} for L''_1H and 1690-1650, 1633 and 1288 cm^{-1} for L_2H which may be ascribed to the stretching vibrations of C=O groups, C=N (imine) and C-O (phenolic) groups, respectively [8-13]. The band at 1633-1622 cm^{-1} due to the stretching mode of the C=N group in the spectrum of the free ligands shows a remarkable negative shift with splittings in the 1595-1612 cm^{-1} region in all the complexes spectra suggesting that the coordinating azomethine nitrogen atoms of the Schiff bases are involved in the complexes formation [8-13]. In the spectra of all the binuclear complexes, the phenolic band at 1260-1269 cm^{-1} is shifted to lower frequency (13-24 cm^{-1}). It is suggested that the oxygen atom of this phenolic (C-O) group is bridge to the metal ions. On the other hand, the IR spectra confirm that the acetate group which may be assigned to (AcO) anion at 1350-1420 cm^{-1} is coordinated [12,15]. As a general remark, a broad band around the 3340-3495 cm^{-1} range is observed in the spectra of L_1H, L'_1H_2 and L''_1H complexes. An additional band at 1160 cm^{-1}, suggests that water molecules are coordinated to metal ions [15,16]. This band may be assigned to water molecule OH stretching frequencies asserting the elemental analysis and thermal studies that the water molecules are involved in the chemical composition of these metal complexes. Moreover, large number of heterocyclic ring vibration at 1580-1200 cm^{-1}. Other band of M-O and M-N bands appear respectively at 540-510, 460-470 cm^{-1}.



a



k= $-OOCCH_3$
y= H_2O
x= -H and - OCH_3

b

Figure 2. Supposed structure of the Cu (II) complexes of the ligands L'_lH_2 (a) and L_lH_2 and L''_lH_2 (b)

3.2. Electronic spectra and magnetic measurements

The electronic spectra were recorded in DMF. In the spectrum of the ligand, the bands in the 390-348 nm range are assigned to the n→π* transitions of the azomethine group. During the formation of the complexes, these bands are shifted to lower wavelength, suggesting that the nitrogen atom of the azomethine group is coordinated to the metal ion. The values in the 320-250 nm range are attributed to the π→π* transition of the aromatic and pyrimidine rings. In the spectra of the complexes, these bands are shifted slightly to lower wavelength.

On the basis of the magnetic data the copper(II) complexes probably has a binuclear structure with phenolic oxygen bridges. The magnetic moment at room temperature of the all the complexes are between 0.7-1.16 B.M. (for per Cu^{+2}), this is abnormally small and consistent with a dimeric structure. The other copper(II) complexes with L_1H, L''_1H and L_2H, a tridentate has been found to have an acetate group in the coordination sphere. However, Cu(II) complexes of the L'_1H_2 and L_2H do not have any groups in the coordination sphere. The electronic spectra of the L_1H and L''_1H copper(II) complexes supported a near octahedral geometry for them and support the proposal that CH_3COO^- and H_2O groups are coordinated axially to Cu(II) ions [12,13]. The reflectance spectrum of the L_1H, L''_1H and L_2H copper(II) complexes exhibit one band at ca. 660 nm which may be assigned to the transition ^2Eg - $^2T_{2g}$ (F) in an octahedral geometry [17]. On the other hand, the reflectance spectrum of the copper(II) complexes of the L'_1H_2 (**a**) and L_2H exhibits a weak transition at ca. 590 nm corresponding to $^2B_{1g}\rightarrow{}^2B_{2g}$ which suggest the presence of a five coordinate geometry [12,17].

Table 2.

Characteristic IR and electronic absorption spectral data of the metal complexes

Compounds	C=O	C=N	C-O	M-N	M-O	λ_{max} (ε_{max}, M^{-1} cm^{-1})
$[Cu_2(L_1)_2(Ac)_2(H_2O)_2]\cdot 4H_2O$	1653 s	1600 m	1266 s	460 w	530 w	666(30), 457(902), 380(1560), 325(1970)
$[Cu_2(L'_1)_2]\cdot H_2O$	1658 s	1610 m	1260 s	465 w	534 w	660(45), 545(65), 428(1816), 325(3602)
$[Cu_2(L''_1)_2(Ac)_2(H_2O)_2]$	1650 s	1610 m	1272 s	470 w	540 w	593(12), 490(850), 440(2140), 329(3828)
$[Cu_2(L_2)_2(Ac)_2]$	1660 s	1598 m	1270 s	460 w	510 w	590(15), 393(1434), 332(2462), 302(3805)

3.3. Thermal Studies

The thermal stability of the complexes was investigated using TGA technique at a heating rate of 10 °C/min in N_2 atmosphere over the temperature range of 25-850.0 °C. In the decomposition process of the Cu(II) complexes, the mass losses corresponded to H_2O, Ph-CH- and the other organic moieties leaving in the first, second, third, fourth and fifth stages of the decomposition, respectively. The three or five stages of decomposition of the all Cu(II) complexes were irreversible. TG studies reveal that complexes suffered loss of H_2O in the first stage in 45-225 ^{o}C and the ligands gradually decompose up to 550-600 ^{o}C. Finally, the complexes decomposed to CuO at higher temperatures [8-12]. It has been found that the complex of L_2H is less thermally stable than other complexes.

4. CONCLUSIONS

A series of binuclear Cu(II) complexes has been synthesized by reacting substituted salicylaldehyde Schiff base derived N-aminopyrimidine. Single crystals of the complexes could not be isolated from any solutions, thus no definitive structure can be described. However, the analytical, spectroscopic, thermal and magnetic data enable us to predict possible structures as shown in Figure 2.

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