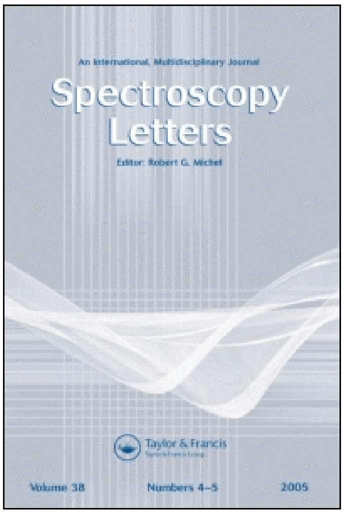

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Comparison of the ht Ultraviolet-Visible Spectra of the Copper(Ii) Complexes of Bidentate Schiff Base Ligands

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COMPARISON OF THE ULTRAVIOLET-VISIBLE SPECTRA OF THE COPPER(II) COMPLEXES OF BIDENTATE SCHIFF BASE LIGANDS

Keywords: Schiff bases, imine, copper complexes, salicylaldimines, ultraviolet-visible spectroscopy

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ABSTRACT

The bis(salicylaldiminato)copper(II) complexes of the ligand series of salicylaldimines derived from the condensation of n-alkyl or n-alkyloxy substituted aromatic amines with 2,4-dihydroxybenzaldehyde were synthesized. A series of Schiff base ligands with the general formula 4-X-N-(2,4-dihydroxybenzylidene)-aniline and differing only in substituents were synthesized. Some of these compounds have already been reported in literature. X=OCH_3[1],OC_2H_5[2],C_4H_9[1]. The copper(II) complexes of these ligands having the general formula, copper,bis[o-[N-(p-X-phenyl)-

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formimidoyl]-4-hydroxyphenolato] were also synthesized. The ligands and their complexes, a total of 24 in number, are studied systematically with ultraviolet-visible spectroscopy to examine the effect of various n-alkyl- and n-alkyloxy substituents on the ligands and on their complexes. In the electronic spectrum of these compounds, the bands observed in the 200-450 nm region which involve charge transfer $\pi-\pi*$ transition were interpreted.

INTRODUCTION

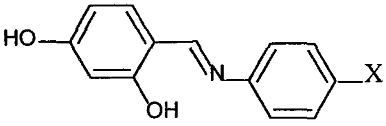
The important place held in coordination chemistry by copper(II) complexes of Schiff base ligands is confirmed by the surveys which are continuously being made. The imines and their copper(II) complexes are colored compounds and they give characteristic absorption bands in the ultraviolet-visible region. Sharma and co-workers, have studied in their published paper the structures of resulting product with the dichlorobis(cyclopentadienyl)titanium(IV) of bidentate imines, derived from salicylaldehyde and 4-substituted aniline, with ultraviolet spectroscopy.

After they recorded the ultraviolet-visible spectra of synthesized complexes in chloroform, they have reported that the bands have occured at about 250 nm, at 320 nm, and at 385 nm, due to $\pi-\pi*$(benzoid), $\pi-\pi*$(azomethine), and $\pi-\pi$ (azomethine) electronic transitions, respectively. For the complexes the first two bands are the same position with ligands, while the third band is shifted to about 425 nm. The bathochromic shift in titanium(IV) complexes of the imines is due to the electrons in nitrogen of the azomethine groups occuring in the bonds nearest to the central metal atoms[3].

Prasad and Sadashiva have synthesized o-hydroxy substituted imines and their copper(II) complexes. They have interpreted the structures of their synthesized compounds by other spectral methods. They studied the structures of the compounds with ultraviolet spectroscopy. The electronic absorption spectra of synthesized compounds have been obtained in chloroform. Their data is below.

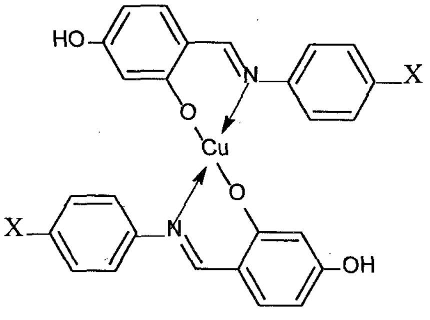
uv-vis $_{max}$ = 352(31,150), 288(15,650) and 250 (19,200) for N-(2-hydroxy-4-phentyloxybenzylidene)-4-n-dodecylphenylaniline.
uv-vis$_{max}$= 389(40,400), 310(56,800) and 259(39,600) for bis-[N-(4-n-dodecylphenyl)-4-n-phentyloxysalicylaldiminato]copper(II)[4].

Jensen has studied the structures of complexes of unsymmetric tetradentate imines with the ultraviolet-visible absorption and has reported that the π–π* transition at 315 nm of the imines is derived from salicylaldehyde shifted towards 285 nm with complexation[5]. In this paper, we wish to present the results of the ultraviolet-visible on copper(II) complexes of a series of salicylaldimine ligands derived from condensation of some aromatic amines with 2,4-dihydroxybenzaldehyde. The structure of ligands is shown as follows



(L)

These ligands are likely to coordinate with bivalent metal ions as shown in the structure as



(CuL$_2$)

In this study, group X is any of the following: H, OCH_3, OC_2H_5, OC_4H_9, OC_6H_{13}, CH_3, C_2H_5, C_4H_9, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$.

EXPERIMENTAL

Materials

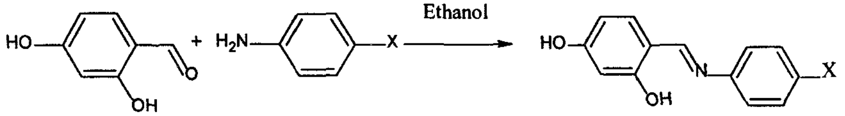
A series of Schiff base ligands and their copper(II) complexes were prepared by a similar procedure. The Schiff base ligands and their copper(II) complexes were synthesized according to the general scheme shown in Figure 1.

The preparation of 4-butoxy-N-(2,4-dihydroxybenzylidene)-aniline and its copper,bis[o-[N-(p-butoxyphenyl)-4-hydroxy]formimidoyl]phenolato] are given as examples.

Step a. Ligand

The 4-butoxy-N-(2,4-dihydroxybenzylidene)-aniline was prepared by adding 2,4-dihydroxybenzaldehyde to the p-butoxyaniline(1:1 molar ratio) in hot ethanol. Water of equal volume was added to the reaction. The reaction mixture was cooled and filtered. Upon concentration and cooling, the ligand

Step a.



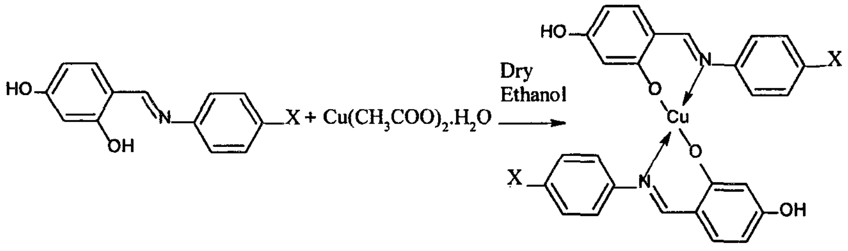
(L)

X= H

X= OC$_n$H$_{2n+1}$ n= 1,2,4,6

X= C$_n$H$_{2n+1}$ n= 1,2,4,6,8,10,12

Step b.



(CuL$_2$)

FIG. 1. Synthetic route for the preparation of the Schiff base ligands and the corresponding copper(II) complexes.

separated out. The ligand was then recrystallized from ethanol, methanol or chloroform[6]. Yield: 59%,yellow, $C_{17}H_{19}NO_3$,285.342 g/mol. MS: m/z [M^+]285, [M^+-C_4H_9]228. ^{1}H NMR($CDCl_3$): δ=8.490(s,>CH=N-),7.259-7.145(m, 2 arom. H on salicylidene ring), 6.889-6.735(m, 2 arom. H on aniline ring), 6.449-6.370(m, 2 arom. H on aniline ring), 3.928-3.882(m, -

$OCH_2(CH_2)_2CH_3$ group), 1.778-1.728(m,$-OCH_2CH_2CH_2CH_3$ group), 1.500-1.446(m, $-OCH_2CH_2CH_2CH_3$), 0.999-0.950(m, $-CH_3$ group). ^{13}C-NMR($CDCl_3$): 169.189(d,>CH=N-), 159.082, 158.897, 141.100(3d, -CH on salicylidene ring), 135.472, 122.376(2d, -CH on aniline ring), 116.399(s, -C on aniline ring), 113.227, 109.527(2d, -CH aniline ring), 105.200(s, -C aniline ring), 69.141(q,$-OCH_2$ group), 14.949(1q, $-CH_3$ on $-OCH_2(CH_2)_2CH_3$ group).

Step b. Complex(II) complex

The copper,bis[o-[N-(p-butoxyphenyl)-4-hydroxy]formimidoyl]phenolato] was prepared by mixing solution of copper(II) acetate monohydrate in ethanol with the solution of 4-butoxy-N-(2,4-dihydroxybenzylidene)-aniline in ethanol, in a 1:2 molar ratio with warming and stirring. The brown compound formed was filtered, washed with ethanol and water and dried[2].Yield=70%, brown, $C_{34}H_{36}CuN_2O_6$, 632.2142 g/mol, [M^+]632, [L+Cu]347.

Apparatus and Techniques

The ultraviolet spectra of Schiff base ligands and their copper(II) complexes were recorded on a Ati Unicam U2-100V 3.00 spectrophotometer and Epson FX-870 Printer. The solvent was of spectrochemical purity, and was used in 10^{-4}-10^{-5} M solutions.

RESULTS AND DISCUSSION

Since all synthesized compounds are soluble in chloroform ($CHCl_3$), this solvent was used for all ultraviolet spectra. The ultraviolet absorption data for the synthesized compounds are given in Tables 1 and 2. The charge transfer $\pi-\pi*$ transition and the π and n transition of their copper(II)

TABLE 1

The ultraviolt-visible transition of the homologue series of the Schiff base ligands

-R or -OR group	benzoid(E1band) $\pi-\pi^*$	azomethine $\pi-\pi^*$	benzoid(E2band) $\pi-\pi^*$	azomethine $n-\pi^*$
H[7]	242	285	300	338
CH_3[7]	243	283	302	341
OCH_3[1]	241	283	302	348
C_2H_5[7]	243	283	301	341
OC_2H_5[2]	241	284	302	348
C_4H_9[1]	241	284	299	342
OC_4H_9[7]	241	285	303	347
C_6H_{13}[7]	241	283	299	341
OC_6H_{13}[7]	241	283	301	349
C_8H_{17}[7]	242	283	302	341
$C_{10}H_{21}$[7]	242	284	301	340
$C_{12}H_{25}$[7]	243	283	300	343

TABLE 2

The ultraviole-visible transition of the homologue series of copper(II) complexes.

-R or -OR group	benzoid(E1band) $\pi-\pi^*$	azomethine $\pi-\pi^*$	benzoid(E2band) $\pi-\pi^*$	charge transfer $\pi-\pi^*$
H[7]	240	258	305	377
CH_3[7]	240	259	306	379
OCH_3[7]	241	260	307	380
C_2H_5[7]	241	261	308	376
OC_2H_5[2]	240	260	307	381
C_4H_9[7]	241	259	306	379
OC_4H_9[7]	241	259	310	370
C_6H_{13}[7]	240	260	307	379
OC_6H_{13}[7]	240	259	309	379
C_8H_{17}[7]	241	259	306	379
$C_{10}H_{21}$[7]	241	259	306	375
$C_{12}H_{25}$[7]	241	260	307	379

complexes and the Schiff base ligands and also, the proton transfer interaction were inspected[1].

Since the azomethine chromophore substitution of the benzene ring causes bathochromic shifts of the B and E2 bands for the synthesized compounds it has been assumed that the E2 bands have caused a longer shift and the B bands are covered by the E2 bands[7]. Substitution of a benzoid system causes a bathochromic shift of the E2 band, which can have two explanations: the conjugation was due to a substituent, or to the electron donating property of the substituent. These results have been explained in another study[7].

4-X-N-(2-hydroxybenzylidene)-aniline general formula and its copper(II) complexes of the imines with the same X group, are used in this work. These compounds have been studied previously with ultraviolet-visible spectroscopy[7]. In this work, the imines and their copper(II) complexes of the structure with 4-X-N-(2,4-dihydroxybenzylidene)aniline, having a second hydroxy group in para- position have been explaned using ultraviolet-visible spectroscopy.

Charge transfer π–π* transitions, using a series of copper,bis[o-[N-(p-X-phenyl)-formimidoyl]phenolato] compounds cause absorption at 385-401 [3], while series of copper, bis[o- [N- (p- X- phenyl)- formimidoyl] -4-hydroxyphenolato] compounds cause absorption at 375-381 nm, thus causing a hypsochromic shift.

As shown in Table 1, the homologue series of Schiff base ligands exhibits a medium band at 242 nm, a weak band at 283 nm, a weak band at 301 nm, and a strong band at 343 nm. These are due to the benzoid (E1band) π–π*,

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[1] The average data as nm are given in the ultraviolet-visible transitions by the calculation of their approximate values.

azomethine π–π*, benzoid(E2 band) π–π*, and azomethine n–π* transitions, respectively. The benzoid (E2 band) π–π* and azomethine n–π* transitions are affected the para substituents of aniline ring. The n-alkyl groups shift the benzoid (E2 band) π–π*, and the azomethine n–π* transitions 1-2 nm and 2-5 nm(bathochromic shift), respectively; while the n-alkyloxy groups cause a shift of 1-3 nm and 9-11 nm, respectively.

Table 2 shows the ultraviolet-visible transition of the copper(II) complexes of Schiff base ligands. The bands at 241 nm, 259 nm, 307 nm, and 378 nm are due to, benzoid (E1 band) π–π*, azomethine π–π*, benzoid(E2 band) π–π*, and charge transfer π–π* transitions, respectively. On complex formation, a hypsochromic shift of 25 nm occurs on the azomethine π–π* transition. In the benzoid(E2 band) π–π* and the charge transfer π–π* transitions, bathochromic shifts occur. A bathochromic shift of 35 nm occurs on the charge transfer π–π* transition.

The benzoid(E2 band) π–π* and azomethine n–π* transitions are affected by the para substituents of aniline ring. While the n-alkyl groups shift the benzoid (E2 band) π–π*, and charge transfer π–π* transitions, 1-3 nm and 1-2 nm (both bathochromic), respectively. The n-alkyloxy groups cause shifts of 2-5 nm and 2-4 nm.

The p-substituted OH group (second oxochrome) in 2-4-dihydroxybenzaldehyde has a dramatice effect on the transitions. A bathochromic shift of 12 nm is observed on the azomethine π–π* transition. The OH group on the aldehyde ring is an oxochromic group without absorption. It is suspected that the unpaired electron of the OH group and the π electron of the ring interact. This action stabilized the π* state, i.e. lowers the π* state energy. This causes a bathochromic shift. The second difference of this series is that the shoulder observed in the other homologue series is not

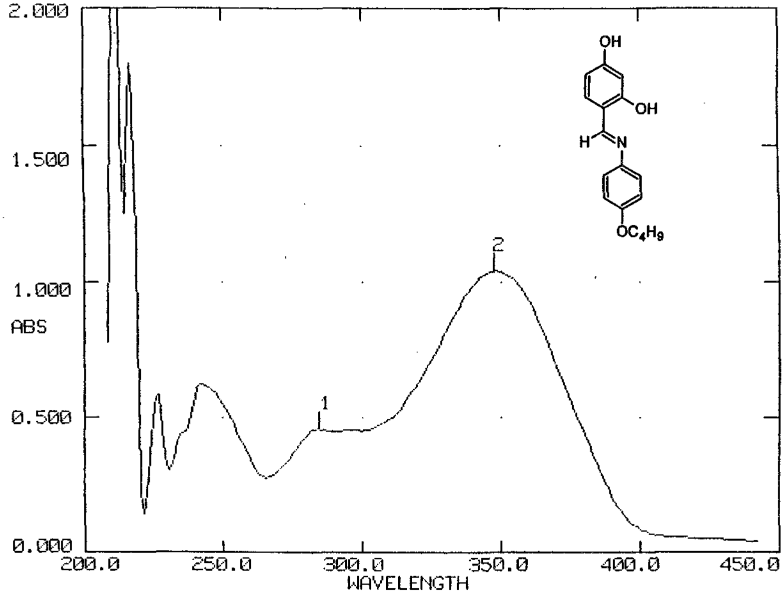

FIG. 2. The ultraviolet-visible spectrum of 4-butoxy-N-(2,4-dihydroxybenzylidene)-aniline

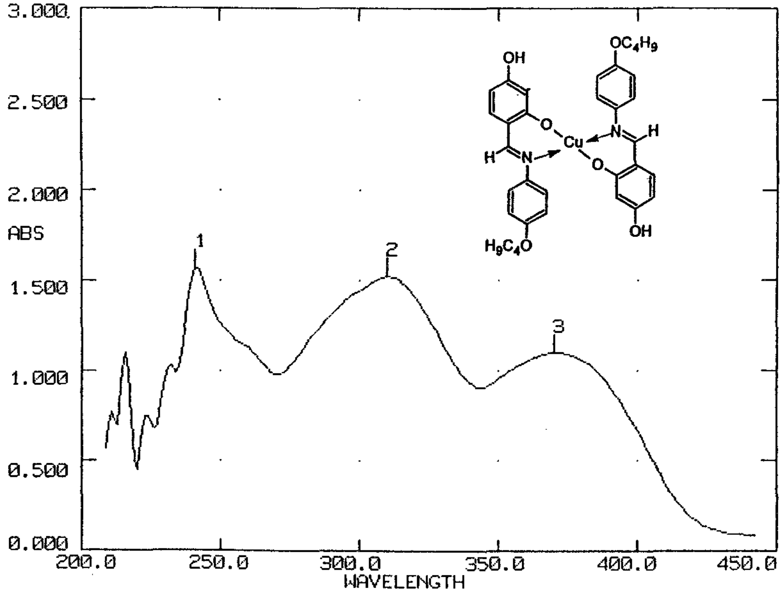

FIG. 3. The ultraviolet-visible spectrum of copper, bis[o-[N-(p-butoxy phenyl) - 4-hydroxy]formimidoyl]phenolato]

observed (see Figure 2). The third difference is the blue shift of the azomethine $n-\pi^*$ transition.

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