

SYNTHESIS AND CYCLIC VOLTAMMETRIC STUDIES OF BIS[5-((4-ALKOXYPHENYL)AZO)- N-(ⁿPENTYL, ⁿDODECYL)-SALICYLALDIMINATO] COPPER(II) COMPLEX HOMOLOGUES

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ABSTRACT: 5-((4-alkoxyphenyl)azo)salicylaldehyde, 5-((4-alkoxyphenyl)azo)-N-(ⁿpentyl, ⁿdodecyl)-salicylalimine and bis[5-((4-alkoxyphenyl)azo)-N-(ⁿpentyl, ⁿdodecyl)-salicylaliminato]copper(II) [alkoxy=OⁿC_nH_{2n+1}; n=3-7] homologues were synthesized and characterized by elemental analyses, mass and IR spectra. All complex homologues are thermally stable. Cyclic voltammetric studies indicated that all copper complex homologues have a quasi-reversible redox wave and peak current ratio (*i*_{pa}/*i*_{pc}) decreasing with increase of alkyl chain length.

KEY WORDS: Schiff base, Salicylalimine, Bis[5-((4-alkoxyphenyl)azo)-N-(ⁿpentyl, ⁿdodecyl)-salicylaliminato] copper(II) homologues, Alkyl chain length.

INTRODUCTION

Schiff base complexes containing different central metal atoms such as Cu, Ni, Co, and Pd have been studied in great detail for their mesogenic properties [1-4], enzymatic reaction, steric effects, and for various crystallographic features [5-8].

Schiff base chelating imines, especially salicylaldimines have been widely used in the preparation of mesogenic complexes. Introducing of alkyl, alkoxy or para substituted benzoyloxy groups in 4- or 5-position of salicylaldehyde ring and condensation of ring substituted salicylaldehyde with linear primary amines

or para-(alkyl, alkoxy, benzoyloxy) anilines, produce salicylalimine ligands which can be chelated with copper(II) in 2:1 ratio (L:M). These compounds exhibit mesophases and show good thermal stability. Due to the diversity of substituents, a great variety of these mesogenic complexes has been reported [9-14].

The structure of some typical organic mesogens contains 4-alkyl or 4-alkoxyphenyl azo groups [15]. In the basic media the latter one can be introduced to the 5-position of salicylaldehyde because of para directing effect of the -OH group.

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Because of the importance of long chain substituted salicylaldehyde Schiff base chelates, we report the synthesis and cyclic voltammetric studies of bis[5-((4-alkoxyphenyl)azo)-N-(ⁿpentyl, ⁿdodecyl)-salicylaldehyde] copper(II) complex homologues.

EXPERIMENTAL

Reagents

All reagents and solvents were used as supplied by Merck. In order to prepare the 4-alkoxyaniline homologues, 4-alkoxy nitrobenzenes were obtained by standard etherification of 4-nitrophenol [16] and reduced to 4-alkoxyanilines [17].

Physical measurements

Elemental (C, H and N) analyses were run on Perkin-Elmer automatic equipment. Electron impact (70 eV) mass spectra were recorded on a Finnigan-mat GC-MS-DS spectrometer model 8430. Infrared spectra were recorded on IR-408 Shimadzu. Voltammetric experiments were carried out in the deaerated (with purged nitrogen) solution of complexes in DMF, containing 0.1M TBAP as supporting electrolyte. All voltammetric studies were carried out with a glassy carbon disc having a diameter of 3 mm as working electrode. A platinum wire electrode was used as auxiliary. An aqueous saturated calomel electrode served as reference and all potentials cited are given versus SCE. Cyclic voltammograms were obtained with an Amel instrument model 2053 as potentiostat associated with a function generator (Amel model 568). In voltammetric measurements freshly distilled reagent grade solvents were used and all experiments were carried out at room temperature. Conductivity measurements were made on Metrohm conductometer model E527 in DMF contain 1 mmol of complexes.

Materials

All homologues of materials were prepared in similar manner. We have substituted the terms aldehyde for homologues of 5-((4-alkoxyphenyl)azo) salicylaldehyde, ligand (n, R) for homologues of 5-((4-alkoxyphenyl)azo) salicylaldehyde-N-alkyl and complex (n, R) for homologues of bis[5-((4-alkoxyphenyl)azo)-N-alkyl-salicylaldehyde] copper (II) complex homologues respectively.

Aldehyde homologues

A 33.5 mmol sample of a freshly distilled 4-alkoxyaniline was dissolved in 15 mL of 6 M HCl at 0-5°C. The reaction flask was immersed in an ice-bath for controlling the temperature. 34 mmol of NaNO₂ was dissolved in 15 mL cold water and added dropwise to reaction mixture over 30 min with constant mechanical stirring. Diazonium salt was obtained and used for coupling to salicylaldehyde.

A 33.5 mmol of salicylaldehyde was added to 15 mL cold NaOH solution (10%) in a 3-necked flask immersed in an ice-bath. Freshly prepared diazonium salt (0-5°C) was added dropwise to the reaction mixture over with constant mechanical stirring. An orange brownish precipitate was formed. During the coupling, temperature of the reaction mixture was kept at 0-5°C. Dilute acetic acid was then added to the reaction mixture. The orange brownish precipitate was filtered off, washed with water and ethanol and recrystallized from ethanol (for n=3-5) and from ethanol/benzene (for n=6,7).

Mass m/e(intensity%); (for n=5): 313.4(30, M+1), 312.4(100, M); (For n=7) 342.4(3.5, M+2), 341.4(58, M+1), 340.4(100, M).

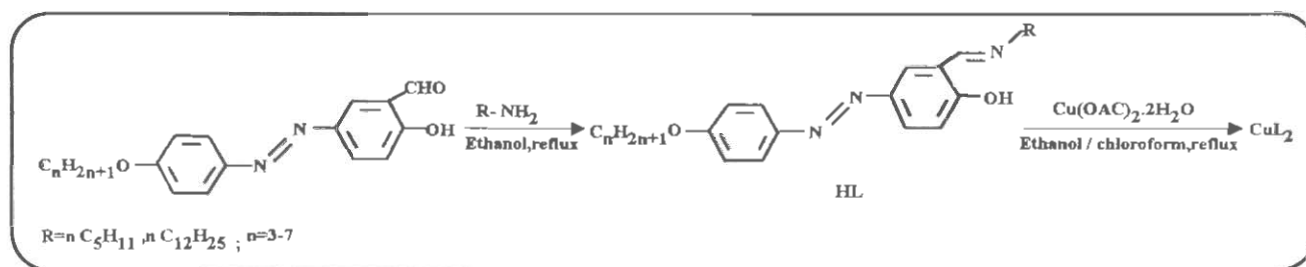
Ligand homologues

Equivalent amount of alkyl amines and aldehyde were condensed by refluxing in ethanol. The orange solution was left at room temperature. Yellow microcrystals (for R= nC₁₂H₂₅; see scheme 1) and yellow flat crystals (for R=nC₅H₁₁; see scheme 1) were formed, filtered off and recrystallized from ethanol/chloroform.

Mass m/e(intensity%): (for n=5, R=C₅H₁₁), 383.6(3.8, M+2), 382(33, M+1), 381.6(57, M); (for n=5, R=C₁₂H₂₅), 480.6(47, M+1), 479.6(47, M); (for n=7, R=C₅H₁₁), 411.7((4, M+2)), 410.7(43, M+1), 409.7(100, M); (for n=7, R=C₁₂H₂₅), 509.8(7, M+2), 508.8(73, M+1), 507.8(100, M).

Complex homologues

A 0.5 mmol sample of ligand homologue was dissolved in 50 mL ethanol/chloroform and to this was added an ethanolic solution of 0.26 mmol cupric acetate dihydrate and the mixture was refluxed for 3 h. The brown solution thus obtained was left at room



Scheme 1

temperature and brown needle crystals were collected by filtration, washed with ethanol and recrystallized from ethanol/chloroform., Analyses Found (Calcu)

R = C₁₂H₂₅ ; n=7; C₆₄H₉₆N₆O₄Cu; C 71.3(71.4), N 8.9(8.93), H 8.5(8.56)

R = C₁₂H₂₅ ; n=5; C₆₀H₈₈N₆O₄Cu; C 71.3(70.73), N 7.9(8.18), H 8.5(8.56)

R = C₅H₁₁ ; n=7, C₅₀H₆₈N₆O₄Cu; C 68.5(68.22), N 9.2(9.55), H 7.9(7.73)

R = C₅H₁₁ , n=5; C₄₆H₆₀N₆O₄Cu; C 66.6(67.03), N 9.9(10.20), H 7.1(7.28)

RESULTS AND DISCUSSION

Preparation of copper(II) complex homologues is shown in Scheme 1. The yields of aldehyde, ligand and complex homologues are given in Table 1. The yields of aldehyde homologues increase with increasing of the alkyl chain length. The yields of salicylaldimine ligands also increase with increasing of n and R.

Melting points of the copper(II) complexes are shown in Table 2. Melting points of the copper(II) complexes regularly decrease with increasing of n and R whereas there are no similar correlations in the ligand homologues and related aldehydes.

Thermal stability of the complexes and ligands were investigated by IR spectroscopy. The compounds were melted and stored in molten phase for several hours. The IR spectra of crystalline compounds and cooled melted compounds did not show any significant difference, thereby these compounds are thermally stable.

The IR spectra of homologue compounds were quite similar. Some selected IR data for new materials are given in Table 3. Disappearance of OH band of free ligands in copper(II) complexes indicated that the OH group has deprotonated and coordinated to the metal ion. On the other hand the C=N stretching mode shifted to a lower frequency by 15 cm⁻¹ upon coordination. These observations and elemental analyses results show that the ligand is coordinated to Cu(II) via N, O in 2:1 ratio. The Cu(II) might be square planar or nearly square planar according to the common stereochemistry of this kind of compounds [3, 20]. The conductivity measurements in DMF shows that the complexes are non-electrolyte.

The cyclic voltammograms of a selected complex are shown in Fig. 1 and detailed cv's in different scan rates are presented in Table 4. In

Table 1 : Yields of the synthesized compounds (%)

n	5-(4-Alkoxyphenyl)azo salicylaldehyde	HA		Cu(A) ₂	
		R=nC ₅ H ₁₁	R=nC ₁₂ H ₂₅	R=nC ₅ H ₁₁	R=nC ₁₂ H ₂₅
3	60	70	76	80	83
4	64	73	78	84	86
5	69	74	78	84	85
6	71	74	78	85	86
7	75	73	80	85	90

Table 2 : Melting points of the compounds (°C)

n	5-(4-Alkoxyphenyl)azo salicylaldehyde	HA		Cu(A)2	
		R=nC ₅ H ₁₁	R=nC ₁₂ H ₂₅	R=nC ₅ H ₁₁	R=nC ₁₂ H ₂₅
3	133-135	63-64	71-72.5	182-184	122.5-124
4	125-127	64-65	68-75.5	171-172	115-117
5	133-134	67-68	72-76	153-156	104-106.5
6	139-141	66.5-67	79-81	148-150	104-105
7	130-132	67-68	71-72	143-145	101-104

potential region between -1000 mV to +1000 mV the free ligand homologues are non-electroactive. Copper complex homologues have a cathodic wave at -674 to -646 mV and related anodic wave at -525 to -569 mV. This redox wave is due to Cu^{II}/Cu^I redox couple [18]. Detailed studies in varying scan rates (50-500 mV/sec) shows that i_{pc} increases linearly (correlation coefficient; $r = 0.9959-0.9982$) with $V^{1/2}$ (scan rate) which indicated the diffusion control process.

Redox process in these complex homologues are quasi-reversible on the basis of ΔE values; 90-121 mV at scan rate of 100 mV/sec; and increase of ΔE values as a function of scan rate [19].

The structure of salicylaldehyde-based Cu(II) bis chelates in the solid state and in solution have been studied in details and are determined to be square planar or nearly square planar [3, 20]. On the other hand it is well known that the quasireversibility of electron transfer is indicative of important stereochemical reorganization [20]. Therefore the quasireversibility of redox process of complex homologues agrees with the planar-to-tetrahedral reorganization following the reduction of Cu(II) to Cu(I) [20].

Increasing the chain length (n and R) causes the decreasing of cathodic and anodic current because of the decrease in diffusion coefficient for complex homologues and increasing of steric effect. On the other hand the peak current ratio (i_{pa}/i_{pc}) decreases with increasing of chain length. It seems that the oxidation of Cu(I) species is more affected by bulky groups because of its tetrahedral coordination geometry, so the peak current ratio is smaller than unity and decrease with increasing of chain length (R and n).

Table 3 : IR data for the synthesized compounds

ν^a	Compound		
	Aldehyde	HL	CuL ₂
OH	3200(m) ^b	3400(m)	—
C-H(Aromatic)	3050(w) ^b	3050(m)	3050(m)
C-H(Aliphatic)	2950(s) ^b	2950(s)	2950(s)
	2850(s)	2850(s)	2850(s)
C=O	1665(s)	—	—
C=N	—	1635(s)	1620(s)
C=C	1600(s)	1600(s)	1600(s)
N=N	1500(s)	1500(s)	1500(s)
C-O(Etheric)	1245(s)	1245(s)	1245(s)
C-O(Phenolic)	1105(m)	1105(m)	1105(m)

a : IR in KBr disk, ν in cm^{-1}

b : s : strong, m : medium, w : weak

Table 4 : Cyclic voltammetry of Copper(II) complex^a (2 mmol in DMF 0.1 M TBAP as supporting electrolyte)

scan rate mV/s	E_{pc} mV	ΔE_p mV	I_{pc} μA	$(I_{pa}/I_{pc})^b$
100	-645	110	41.05	0.89
200	-657	137	56.84	0.88
300	-672	160	67.37	0.86
400	-688	181	78.94	0.86
500	-698	197	88.42	0.86

a : R = C₅H₁₁, n=3; GC electrode

b : The Nicolson equation was used [19]

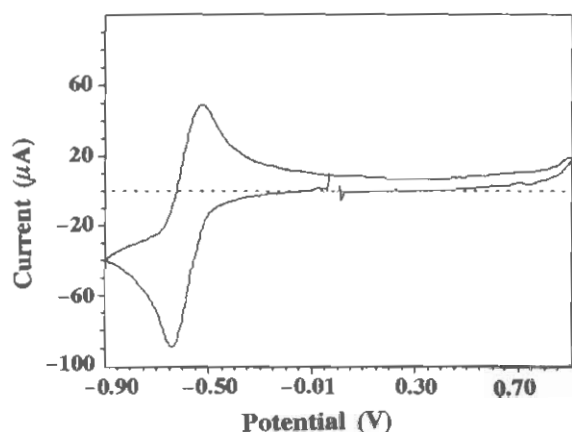


Fig. 1: Cyclic voltammogram of bis[5-((4-alkoxyphenyl)azo)-N-(R)-salicylaldiminato] copper(II), $R=C_5H_{11}$, $n=3$ (4 mmol) in DMF and 0.1 TBAP as supporting electrolyte; scan rate 100 mV/sec other cv's are quite similar.

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