SYNTHESIS, CHARACTERIZATION AND ELECTRO-CHEMICAL BEHAVIOUR OF 4-(4-NITROPHENYL-AZO)-2-(2-METHOXY PHENIMINO)-PHENOL AND ITS Ni(II), Cu(II), Co(II) and Fe(III) COMPLEXES

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ABSTRACT: *4-(4-Nitrophenyl-azo)-2-(2-Methoxy phenimino)-phenol and its coordination compounds with Ni(II), Cu(II), Co(II) and Fe(III) have been synthesized and characterized by elemental analyses, FT-IR, Far-IR, Near IR, UV-Vis, Mass Spectrometry and Molar Conductivity and their electrochemical behaviours are reported.*

KEY WORDS: *Chromophore, Schiff base, Co(II), Ni(II), Cu(II) and Fe(III) complexes.*

INTRODUCTION

In recent years considerable interest has been shown in the synthesis of new materials with NLO (Non Linear Optical activity) properties which have applications in Laser technology, telecommunications and integrated optical devices [1-4].

Non-centrosymmetric, highly polarizable organic and organometallic conjugated molecular systems bearing a donor group ($-N(CH_3)_2$, $-OCH_3$, $-NH_2$,...) at one end and an acceptor group($-CN$, $-NO_2$, $-CHO$, ...) at the other end have been shown to produce materials displaying large macroscopic nonlinearity [5-8].

We report here the synthesis of a new chromophore and its schiff base with ortho-anisidine and the schiff base complexes with Co(II), Ni(II), Cu(II) and Fe(III) ions.

EXPERIMENTAL

Physical Measurements

UV-Vis spectra were obtained using a Shimadzu (UV-265 FW) spectrophotometer in the 14000-50000 cm^{-1} region in dimethylsulphoxide (DMSO) solution.

FT-IR spectra were recorded on a Shimadzu FT-IR 8101M spectrophotometer. Using KBr discs in the 400-4000 cm^{-1} region. Far-IR spectra were recorded on a Perkin-Elmer model 883 spectrophotometer, using CsI discs in the 200-600 cm^{-1} region.

Near IR spectra were recorded on a model 750 Mgna

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Nicolet FT-IR spectrophotometer. Mass spectra were recorded on a MAT 311, Varian spectrometer. Carbon. Hydrogen and Nitrogen analyses were performed in a Perkin-Elmer analyzer. Iron , Nickel , Copper and Cobalt were measured in a Shimadzu atomic absorption spectrophotometer model A-670G. Molar conductivities were obtained with a E 527 Metrohm conductometer, using DMF as solvent at 20°C.

The cyclic voltammograms of compounds in DMSO (~0.004 M) containing 0.1 M tri(n-butyl) ammonium perchlorate as supporting electrolyt were taken on a model 568 AMEL instrument.

A single compartment cell was imployed with an SCE reference electrode, a platinum wire counter-electrode and a glassy carbon (3 mm outer diameter) as working electrodes. The scan rate was 100 mV s^{-1}.

Materials

All reagents and solvents were analytically pure reagent grade and were from Merck.

Synthesis of ligand HL

In order to prepare the ligand HL, 5-(4-nitro-phenyl-azo)-salicylaldehyde (I) was prepared in two steps:

i) Diazonium salt was prepared by adding sodium nitrite to prepared *p*-nitroaniline hydrochloride [4].

ii) In a three-necked flask 5.3 mL of salicylaldehyde in 50 mL of sodium hydroxide 10% was dissolved and a red solution appeared. The cold diazonium salt solution was added dropwise to the red solution. This mixture was stirred untill a yellow color precipitate appeared. The reaction temperature was controlled in the range of -5 to 0°C for 1 h. The precipitate was filtered and washed with water and recrystalized from absolute ethanol, yield 74%, mp 205°C.

In order to prepare (HL), to a hot solution of 2.7 g (0.01 M) 5-(4-nitro phenyl-azo)-salicylaldehyde in 20 mL of 1:1 mixture of dichloromethane and absolute ethanol was added 1.12 mL (0.01 M) of *o*-anisidin in 10 mL of ethanol and the mixture was then slowly refluxed for 2 h at 80°C. The mixture was cooled down to room temperature, bright dark-red crystaline compound separated out, which were collected by filtration, washed well with ethanol and dried in vacum.

All these steps in preparing of (HL) are shown in scheme 1. The product was recrystalized from hot absolute ethanol and dichloromethane in ratio of 1:1. Yield 70%, mp 220°C. Found: C, 63.4; H, 4.2; N, 14.8; $C_{20}H_{16}O_4$ requires: C, 63.8; H, 4.3; N, 14.9.

Synthesis of complexes

A solution of $M(O_2CCH_3)_2 . 4H_2O$ (1 mmol), [M= Co(II), Ni(II), $CuCl_2$ or $FeCl_3 . 3H_2O$ (1 mmol) in absolute ethanol (20 mL) were added dropwise with stirring to a solution of HL (1 mmol) in dichloro-metane (25 mL). The reaction mixture was heated under reflux in a water bath at 85°C for 2 h and then filtered. The precipitate was washed three times with hot ethanol until the filtrate became colorless, and dried to constant weight at 100°C. Dark coordination compounds obtained, yield >70%.

RESULTS AND DISCUSSION

The elemental analyses results and some of physical properties of prepared compounds are given in Table 1.

The results show that the ligand HL coordinates to metal ions with molar ratio of 1:1. The purity of (HL) was confirmed by Mass spectrum; m/z (cal.) 376.4, m/z(found) 376.8.

The structural determination of HL by Mopac computational program shows the three donor atoms of HL [O, N, O as seen in Scheme (1)] are coplaner. The torsional angles of 1-2-3-4,5-6-7-8 and 3-4-5-6 are 0.000, 0.000 and 180.000 respectively.

The important FT-IR absorption frequencies (cm^{-1}) of I, HL and its coordination compounds are listed in Table 2.

The FT-IR spectra of the coordination compounds clearly changed compared with that of HL. In the FT-IR spectra of coordination compounds ν_{O-H} disappeared and the bands of ν_{C-N} and ν_{O-CH_3} shifted to the lower frequencies by 8-15 cm^{-1}. Therefore the HL acts as a three dentate ligand in these complexes [10]. The formation of M-O and M-N is also comfirmed by Far-IR spectrum of the complexes [11].

The important assignments (cm^{-1}) of Far-IR spectra of complexes are listed in Table 3. The $[CoL(OOCCH_3)]$ spectrum shows a broad band at 411 cm^{-1} and $[NiL(OOCCH_3)]$ complex shows two bands at 408 and 427 cm^{-1} for M-O bonds [11].

The appearance of two bands at 1575, 1410 cm^{-1} and 1578, 1410 cm^{-1} in FT-IR spectra of [NiL-$(OOCCH_3)$] and [Co L$(OOCCH_3)$] complexes respectively indicates that the $(CH_3COO)^-$ acts as a monodentate ligand [11].

The equal heights of corresponding peaks of cyclic voltamograms of metal salts and their relative complexes in DMSO under the same conditions are suggestive of monomeric molecular structure for all prepared complexes.

Table 1 : The elemental analysis and some physical properties of the ligand (HL) and its coordination compounds.

Compounds	Molecular weight	mp (°C)	Colour	Elemental analysis(%)[a]			
				C	H	N	M[(b)]
HL($C_{20}H_{16}N_4O_4$)	376.40	220	red	63.4(63.8)	4.2(4.28)	14.8(14.88)	—
[CuLCl]	474.36	350[c]	brown	51(50.7)	3.4(3.2)	12(11.8)	13.3(13.4)
[CoL($OOCCH_3$)]	493.34	356[c]	brown	53.5(53.3)	3.8(3.7)	11.8(11.4)	12(12.1)
[NiL($OOCCH_3$)]	493.09	380[c]	red-brown	53.5(53.5)	4(3.7)	11.6(11.4)	9.2(9.6)
[$FeLCl_2$]	502.12	300[c]	dark-brown	48(47.8)	3.3(3)	10.8(11.1)	11.1(10.7)

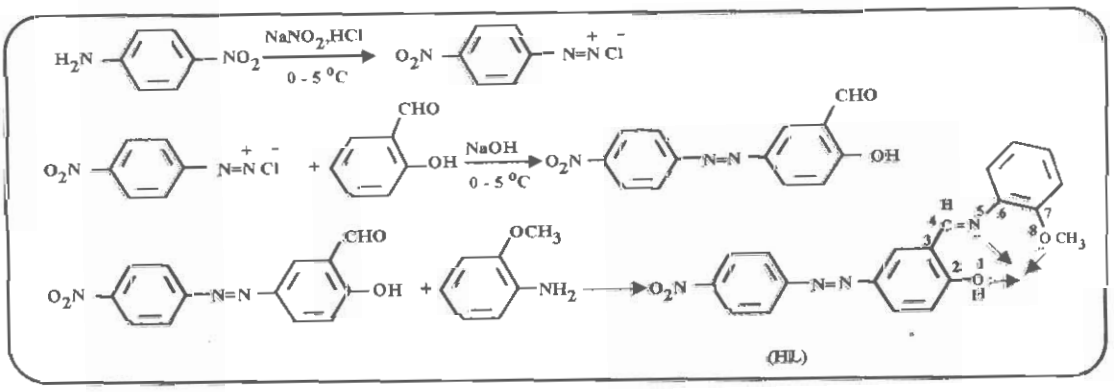
a) Calculated values are given in parentheses

b) M shows the metal ion of the complexes

c) Decomposed

Table 2 : FT-IR assignments of HL and its coordination compounds (cm^{-1})

Compound	O-H	C-H (arom.)	C-H (aldeh.)	C=O	C=N	C=C	N=O (assym.)	N=N	N=O (symm.)	C-H (CH_3 bond)	C-O	C-N
I	3400	2800	2800	1666.8	—	1608.9	1529.9	1420	1346.5	1377	1220	854.6
	3200					1479						
HL	3420	2900	2837	—	1624.3	1591	1522	1420	1338	1375	1252	858
						1466						
[CoL($OOCCH_3$)]	—	2900	2800	—	1607	1583	1518.2	1419	1335	1377.8	1242.4	856
[NiL($OOCCH_3$)]	—	2900	2800	—	1612.7	1585.7	1520	1419.8	1335	1377.4	1238.5	854
[CuLCl]	—	2900	2800	—	1616.6	1587.7	1508.6	1421.8	1342	1385	1244.3	—
[$FeLCl_2$]	—	2900	2800	—	1608.9	1585.7	1520.1	1420	1340.7	1385	1238.5	854.6



Scheme 1

Table 3 : The important assignments of Far-IR spectra of complexes (cm^{-1})

Complex	M-Cl	M-O	M-N
[CuLCl]	315	414	357
[$FeLCl_2$]	319	416	361
[$CoL(OOCCH_3)$]	—	411(broad)	355
[$NiL(OOCCH_3)$]	—	408, 427	358

The UV-Vis absorption bands of compounds in the region of 14000-50000 cm^{-1} are given in Table 4. The UV-Vis spectrum of I shows three-bands at 27840, 37313 and 43937 cm^{-1} which are tentatively assigned to the $n \rightarrow \pi^*$ transition of –N=N–, $-NO_2$ and >C=O groups respectively [11]. HL also shows three bands at 26343.5, 35600 and 39154 cm^{-1}. The shifts of (I) bands in comparison with those of HL could be due to increasing conjugation of the π-system [12,13].

Table 4 : UV-Vis absorption bands of I, HL and coordination compounds.

Compound	Characteristic bands(nm in DMSO)			
	1	2	3	4
I	21231*	27840	37313	43936
HL	20833*	26343	35714	39154
[CuLCl]	20833*	26315	36363	38550
[$FeLCl_2$]	20618*	26766	36363	38789
[$CoL(OOCCH_3)$]	20408*	26330	36023	38880
[$NiL(OOCCH_3)$]	20903*	29104	35868	39062
	23256	29890		

* *With shoulder*

The >C=O band of I at 43937 cm^{-1} disappeared in HL spectrum. The appearence of a new band at 39154 cm^{-1} seems to correspond to formation of imine >C=N-bond in HL. The UV-Vis spectra of I and HL were also recorded in absolute ethanol and dichloromethane. The comparison of these spectra with the corresponding spectra in DMSO shows about 5 to 10 nm shifts in positions of bands. I and HL are insoluble in hexane, but in it their colour change from yellow to dark-brown and from red to orange-red respectively. As a result of this solvatochromic behaviour of I and HL, they are currently screened for second-harmonic generation (SHG) [14, 15].

The appearence of UV-Vis spectra of HL and complexes are similar in the 14000-50000 cm^{-1} region except in the case of [$NiL(OOCCH_3)$] which shows two more intense bands. These two bands may corresponds to charge transfer bands [16]. Solid state reflectance of [$NiL(OOCCH_3)$] also shows two broad intense bands at 7500 and 10200 cm^{-1} and since donor atoms of HL(O, N, O) are coplanar and there is no counter anion in the complex, we may suggest a square planar structure for [$NiL(OOCCH_3)$] [16].

In the case of [$FeLCl_2$] no d-d or charge transfer can be observed in the UV-Vis region, but in the solid state reflectance spectra in the near-IR region, the complex shows a very weak but sharp band at 7167 cm^{-1}. Therefore a trigonal bipyramidal structure may be suggested [17]. Since the donor atoms of ligand are coplanar it may be suggested that two oxygene atoms of HL occupies axial positions of the bipyramid structure.

The appearence of two broad peaks in the solid state reflectance spectrum of [$CoL(OOCCH_3)$] in the region of 7200-12000 cm^{-1} suggests a pseudotetrahedral structure [16].

The solid state reflectance spectrum of [CuLCl] shows a very broad band in the range of 8000-16000 cm^{-1}. Therefore a compressed tetrahedral geometry may be suggested to the complex [16].

The molar conductances of HL and coordination compounds in DMF (mho cm^2 mol^{-1}) at 20°C with concentrations of 10^{-3} M are listed in Table 5. The molar conductances are in the region of 6.28-1.80 mho cm^2 mol^{-1} due to the fact that ligand and coordination compounds are very weak electrolytes (the

Table 5 : Molar conductance of the ligand and coordination compounds in DMF (mho $cm^2 mol^{-1}$) at 20°C.

Formula	HL	[CuLCl]	[$NiL(OOCCH_3)$]	[$CoL(OOCCH_3)$]	[$FeLCl_2$]
(mho cm^2 mol^{-1})	6.25	4.05	1.80	2.84	2.09

Table 6 : Peak potential of free ligand and ingaged ligand in the complexes.

Compound	HL	[CuLCl]	[NiL(OOCCH$_3$)]	[CoL(OOCCH$_3$)]	[FeLCl$_2$]
E_p^c(mV)	-756	-760	-802	-811	-882
d^n	—	d^9	d^8	d^7	d^5

Table 7 : Peak potentials of compounds vs SCE (E_p mV) of the complexes and their corresponding salts

Compound	M^0/M^I	M^I/M^0	M^I/M^{II}	M^{II}/M^I	M^{II}/M^{III}	M^{III}/M^{II}	M^0/M^{II}	M^{II}/M^0
$CuCl_2$	158.8#	-1230#	509#	26#	1058*			
[CuLCl]	5#	-1070#	431#	219#	831*			
$FeCl_3$					-23#	311#	-200#	-1650#
[FeLCl$_2$]					-11#	265#	-584#	-1600#
Co(OOCCH$_3$)$_2$					960*		116.6#	-1320#
[CoL(OOCCH$_3$)]					878*		141#	-1480#
Ni(OOCCH$_3$)$_2$					1053*		56#	-2120#
[NiL(OOCCH$_3$)]					932*		29#	-1900#

* *Irreversible* # *Quasi-reversible*

reference values for 1:1 electrolytes have taken as 65-90 mho cm^2 mol^{-1} in DMF) [18].

Experimental results show that Cu(II), Ni(II) and Co(II) ions in the complexes are four coordinated. Since L^{-1} acts as a tridentate ligand, the fourth coordination position is occupied by the metal salt anion. In the case of Fe(III), the complex is five coordinated, the other two coordination positions of Fe(III) are occupied by two chlorides.

The electrochemical properties of HL, complexes and their corresponding salts [$CuCl_2$, Co(OOCCH$_3$)$_2$, Ni(OOCCH$_3$)$_2$ and $FeCl_3$] were investigated by using cyclic voltammetry in DMSO with tri(n-butyl) ammonium perchlorate as supporting electrolyte. HL has a well defined cathodic irreversible peak at -756 mV. The comparison of HL and HL'(HL without NO_2) cyclic voltammogrames indicates that both cathodic and anodic peaks in HL cyclic voltammogram correspond to NO_2 group. The cathodic peak (at -756 mV) shifts to lower potentials in complexes, as the number of d-electrons of metal ions decrease. The relevant cathodic potentials are reported in Table 6. It seems that metal ions in complexes cause this shift via the π-conjugation system in the ligand. Thereby these compounds could have NLO properties. Comparison of peak potential of [FeLCl$_2$] with those of three other complexes shows that the oxidation state of metal ion has more effect on the peak potential than d^n configuration.

The comparison of peak potentials of metal ions in complexes with those of corresponding salts show that complexation of metals shifts the peak potentials (Table 7). In the case of [CuLCl] and [FeLCl$_2$] the reversibility of Cu(II)/Cu(I), ($\Delta E_p = E_{pa} - E_{pc} = 212$ mV, $i_{pa}/i_{pc} \approx 0.9$) and Fe(II)/Fe(III), ($\Delta E_p = E_{pa} - E_{pc} = 276$ mV, $i_{pa}/i_{pc} \approx 0.5$) systems increase compared with their corresponding slats. The anodic wave for [CuLCl] and $CuCl_2$ at 257 and 314 mV respectively at 100 mV s^{-1} scan rate, disappeares at 200 mV s^{-1} scan rate.

This anodic peak may be related to three coordinated Cu(I) complex, which is unstable species [19]. The cyclic voltammograms of HL and its complexes are given in Fig. 1.

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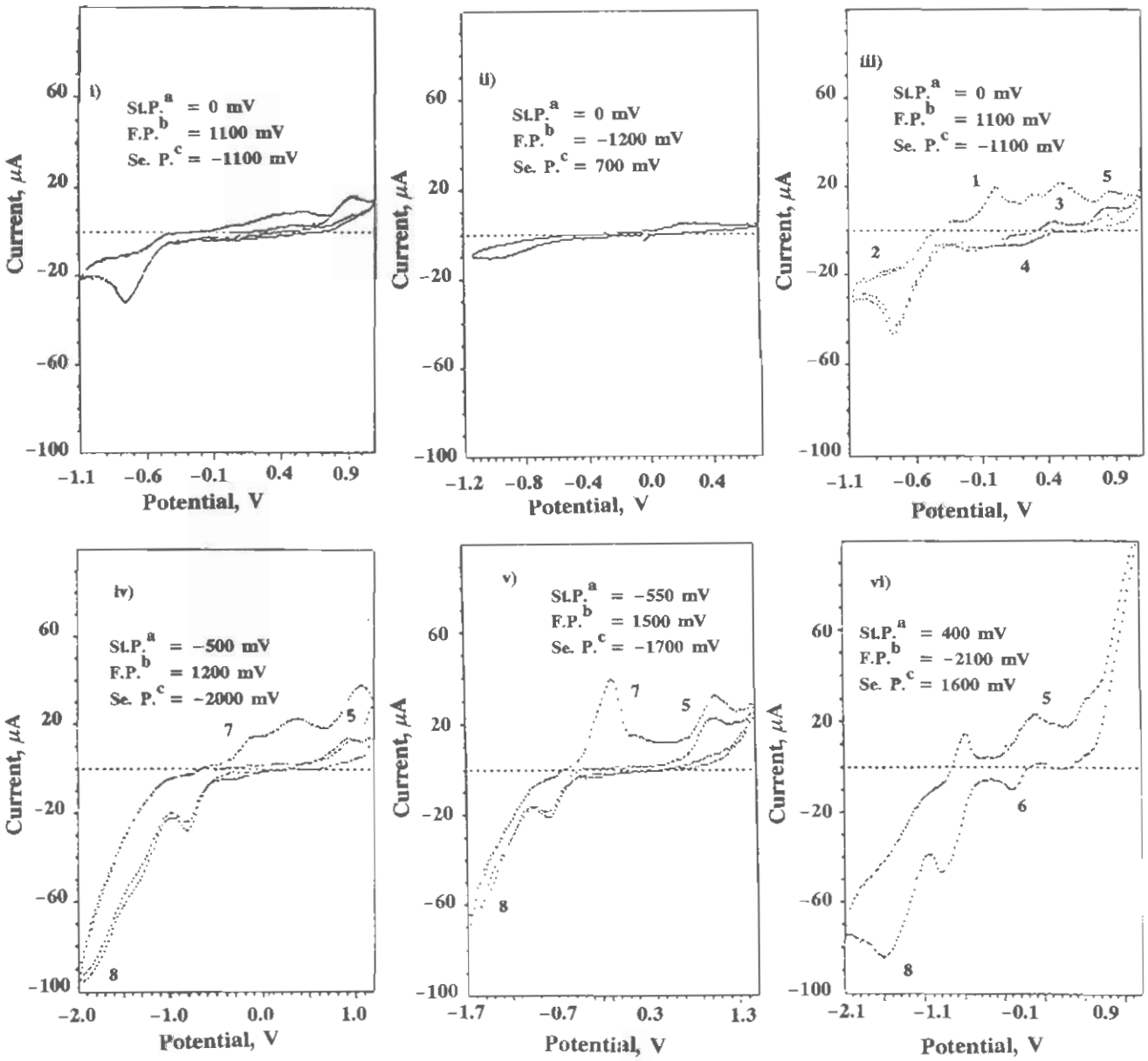

Fig. 1: Cyclic voltamograms recorded at GC electrode on a DMSO solution containing $[(n\text{-}Bu)_3NH][ClO_4]$ (0.1 mol/L); vs SCE, Scan rate: 100 mV/s, i) HL, ii) HL', iii) $[CuLCl_2]$, iv) $[NiL(OOCCH_3)]$, v) $[CoL(OOCCH_3)]$, vi) $[FeLCl_2]$.
The numbers of peaks indicate: 1, M^0/M^I; 2, M^I/M^0; 3, M^I/M^{II}; 4, M^{II}/M^I; 5, M^{II}/M^{III}; 6, M^{III}/M^{II}; 7, M^0/M^{II}; 8, $M^{II}/M.^0$ (The peak potentials are given in Table 7). a; start potential, b; first potential, c; second potential.

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