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STRUCTURAL, OPTICAL AND FLUORESCENCE PROPERTIES OF AZO SCHIFF BASED METAL COMPLEXES

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ABSTRACT

Azo compounds are highly important, well known and widely used substances in the textile, paper, coloring agents for foods and cosmetics industries. Other applications include emerging technologies like liquid crystals, organic photoconductors and non-linear optic. The field of NLO and photonics are rapidly emerging as the technology for the 21st century . Photonics is the technology in which a photon instead of an electron is used to acquire, store, process and transmit information. The synthesized complexes are characterized by magnetic susceptibility measurements, molar conductance, elemental analysis and spectral analysis (IR, UV-Vis, ^{1}H-NMR, EPR and EI-mass). The photoluminescence properties of azo Schiff base ligand and its metal complexes were studied at room temperature in ethanol. Metal mediated fluorescence enhancement is observed on complexation of the azo Schiff base ligand. The second harmonic generation efficiency and solvatochromic behaviors of the azo Schiff base ligand was studied and also the surface morphology of the Cu(II) complex was examined by Scanning Electron Microscopy. The Non Linear Optical properties of the ligand are expected to result in the realization of advanced optical devices in optical fibre communication (OFC) and optical computing.

Key words: Fluorescence, Metal complexes, Optical properties

I. INTRODUCTION

Azo compounds are a pair of symmetrically or asymmetrically substituted nitrogen atoms that are connected by a double bond [1]. The research of azo compounds has now been expanded to evaluate the potential as functional components in catalysis, as optical storage media, in supramolecular chemistry and in polymer chemistry [2-4]. Besides, azo compounds are important analytical aid compounds serving as pH indicators, complexometric indicators and to a lesser extent, pre-concentration reagents.

Non Linear Optics (NLO) deals with the interactions of applied electromagnetic fields in various materials to generate new electromagnetic field altered in phase, frequency, amplitude or other physical properties [5]. The field of NLO and photonics are rapidly emerging as the technology for the 21st century [6]. Photonics is the technology in which a photon instead of an electron is used to acquire, store, process and transmit information. Replacing electronic by photonic technologies needs materials with optimized optical performance and chromophores with increased nonlinear optical (NLO) response. Materials with increased NLO properties are thus widely investigated in material sciences [7,8]. NLO effects are of major importance for optical data processing, transmission, storage, and for ultrafast image-processing, making such systems valuable materials for communication systems and computers. Azo compounds, having conjugated electronic structures and containing substituents on the aromatic rings with push-pull electron ability [9] shows large optical nonlinearity, which have been viewed as new candidates in electro-optic application. In general, these reactions produce remarkable changes of the dipole moments of these molecules leading to photo induced optical birefringency [10,11]. Hence with an aim of studying the Non linear optical property, fluorescence property and Solvatochromic behaviour azo Schiff base ligands and complexes have been synthesized and characterized.

II. EXPERIMENTAL

The chemicals and solvents were purchased from Aldrich Chemical & Co. and the solvents were purified by standard methods. Elemental analyses were carried out using a Perkin-Elmer 2400 II elemental analyzer. Molar conductance of the complexes was measured in DMSO at room temperature using a Systronic Conductivity Bridge 304. Magnetic susceptibility of the complexes was performed on a Sherwood MSB mark1 Gouy balance. Infrared spectral studies were carried out on a Shimadzu FT IR 8000 spectrophotometer using KBr discs. UV-Vis spectra were obtained using a THERMO SPECTRONIC 6 HEXIOS α. NMR spectra were recorded on Bruker DRX-300, 300MHz NMR spectrometer using TMS as reference. ESR spectra of the Cu(II) and VO(II) complexes were recorded in Varian E-112 machine at 300 and 77 K using TCNE (Tetracyanoethylene) as the g-marker. The second- harmonic generation (SHG) conversion efficiency of the Schiff base ligands were determined by the modified version of powder technique in IISc, Bangalore. XRD of copper complex was recorded using OCPL/ARD/26. Emission spectra in the UV-Visible range were recorded on Elico SL174 Spectra Treats Version 3.0 spectrophotometer between 200-900 nm by using suitable solvent at Lady Doak College, Madurai.

SYNTHESIS OF LIGANDS

Ligand-1: An ethanolic solution (20 mL) of 5-((4-chlorophenyl)diazenyl)-2-hydroxybenzaldehyde (**L1**) [12] (2.6 g, 10 mmol) was added to an ethanolic solution of diaminomaleonitrile (0.54 g, 5 mmol). The solution mixture was refluxed with a few drops of glacial acetic acid as catalyst for 8 h. The resulting brown solution was cooled in ice to give brown precipitate, which was collected by filtration and dried under vacuum. Recrystallization from absolute ethanol gave brown solid. The overall yield varied between 60~70 %. m.pt. 229-231 °C. The scheme is depicted as follows **Fig.1**.

Ligand-2: Azo Schiff base ligand (**L2**) was prepared by adding equimolar amount of 5-((4-chlorophenyl)diazenyl)-2-hydroxybenzaldehyde (2.60 g, 10 mmol) in 10 mL of ethanol to 2-hydroxybenzohydrazide (HBHZ) (1.52g, 10 mmol) in 10 mL of ethanol. The mixture was refluxed while stirring for 2 h. The formed bright yellow colour solid product was filtered off, washed with ethanol several times followed by recrystallization from ethanol and finally dried under vacuum. The yield obtained was 50 – 60 %, m.p. 286-288 °C. **Fig. 2**

SYNTHESIS OF METAL(II) COMPLEXES

A solution of metal(II) chloride/sulphate ($NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2.2H_2O$) in ethanol (1 mmol) was stirred with an ethanolic solution of L_1 and L_2 (0.5 g, 1 mmol) in the presence of 1mmol of NaOH on a magnetic stirrer. On concentration, the solid complex precipitated was filtered, washed thoroughly with ethanol and dried in vacuum. **Fig. 3,4.**

III. RESULTS AND DISCUSSION

The analytical data and physical properties of novel Schiff base Ligands L_1 and L_2 and their metal(II) complexes are in good agreement with calculated values **Table 1, 2.** The molar conductance of the complexes implies that the complexes are non-electrolytes. Analytical data are in good agreement with calculated values, as expected for the assigned formula, [ML], where M = VO(II), Mn(II), Co(II), Cu(II) and Zn(II) and $[ML(H_2O)_2]$ for Ni(II) complex of Ligand 1. The analytical data of the complexes are consistent with the general formula $[ML(H_2O)]$, where M = VO(II), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) for Ligand 2.

IR SPECTRAL STUDIES

The IR spectra provide valuable information regarding the nature of functional group attached to the metal atom. In order to study the binding mode of the ligand to metal in the complexes, the IR spectrum of the free ligand was compared with the corresponding metal complexes. Selected vibrational bands of the ligand L1 and L2 and its metal complexes and their assignments are listed in **Table 3, 4** which confirms the structural geometry of the ligands and theirs complexes [12-17].

^{1}H-NMR SPECTRAL STUDIES

The ^{1}H NMR spectra of the azo Schiff base Ligands L1 and L2 and its zinc(II) complex in DMSO-d_6 were recorded. The stoichiometry of the compound is determined by recording the chemical shifts of the hydroxyl protons and the HC=N protons of the synthesized compounds. The two hydroxyl groups and azomethine groups are in equivalent environment in the present ligand and its complexes. The ^{1}H-NMR spectrum of the Schiff base ligand shows the following signals: phenyl as multiplets around 6.8 to 7.9 δ, the peak at 10.0 δ is attributable to the phenolic –OH group present in the salicylaldehyde moiety, the azomethine proton (–CH=N–) appears at 8.2 δ. Zinc complex shows that the phenolic -OH is involved in complexation due to the disappearance of the signal at 10.0 δ. The azomethine proton signal in the spectrum of the zinc complex is shifted downfield compared to the free ligand, suggesting deshielding of the azomethine group due to the coordination with metal ion. There is no appreciable change in all of the other signals of this complex . The ^{1}H-NMR spectrum of the azo Schiff base in DMSO-d_6 is shown in **Fig. 5**

FLUORESCENCE STUDIES

The photoluminescence properties of azo Schiff base ligand and its metal complexes were studied at room temperature in ethanol. The emission spectrum of the ligand excited at 361 nm show an emission peak at 359 nm. The metal complexes show strong fluorescence with moderate quantum yield excitation at 480 – 546 nm gives an emission at 479 - 540 nm, assigned to $\pi - \pi^*$ intraligand fluorescence. It is interesting that the complexes show a higher intensity than that of the free ligand **Fig.6.** This is supported from their calculated quantum yield values with reference to quinine sulfate. Metal ions can enhance or quench the fluorescence emission of some Schiff base ligands containing an aromatic ring. Quenching of fluorescence of a ligand by transition metal ions during complexation is a rather common phenomenon which is explained by processes such as magnetic perturbation, redox activity, electronic energy transfer.[18-21].

SOLVATOCHROMIC BEHAVIOR

The physical and chemical properties of organic molecules utilized in different scientific and technological applications can strongly depend on the properties of surrounding media. The prominent electronic absorption and solvatochromic effects observed in the present investigated azo compound indicate that the compound have NLO response. The nature of π conjugated system, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions of –N=N- and –CH=N- moieties are responsible for the solvatochromic behaviour of the ligand **Fig.7**. The solvatochromic behavior of the compounds is generally considered as indicative of high molecular hyperpolarisability and potential NLO properties. The prominent electronic absorption and solvatochromic effects observed in the present investigated azo compound indicate that the compound have NLO response.[22,23]

NONLINEAR OPTICAL PROPERTIES

The SHG (second harmonic generation) efficiency of the azo Schiff base ligand1 & 2 were determined by modified version of powder technique developed by Kurtz and Perry. The efficiency of the sample was compared with microcrystalline powder of KDP and urea. The input energy used in this particular setup is 2.2 mJ/ pulse. The experimental data infers that the ligand shows 2.6 and 3.1 times more active than that of the activity of urea and KDP. The result indicates that the presence of strong electron donating hydroxyl group in the phenyl ring increases the Second Harmonic Generation (SHG) responses. From comparisons of the NLO activity of the ligand under investigation (CDHBHZ, **L$_2$**), with those of azo Schiff bases (**L$_1$)** one may conclude that the presence of –OH group on the phenyl ring increases the noncentrosymmetric character of salicylaldiminato ligands and may also cause the π electrons to be more delocalized and therefore enhances the second-order nonlinear optical property of these compounds [24].

IV. FIGURES AND TABLES

Fig-1 Synthesis of Ligand-1

Fig-2 Synthesis of Ligand-2

Fig. 3 Structure of the metal(II) complexes of L_1)

Fig. 4 Structure of the metal(II) complexes of L_2)

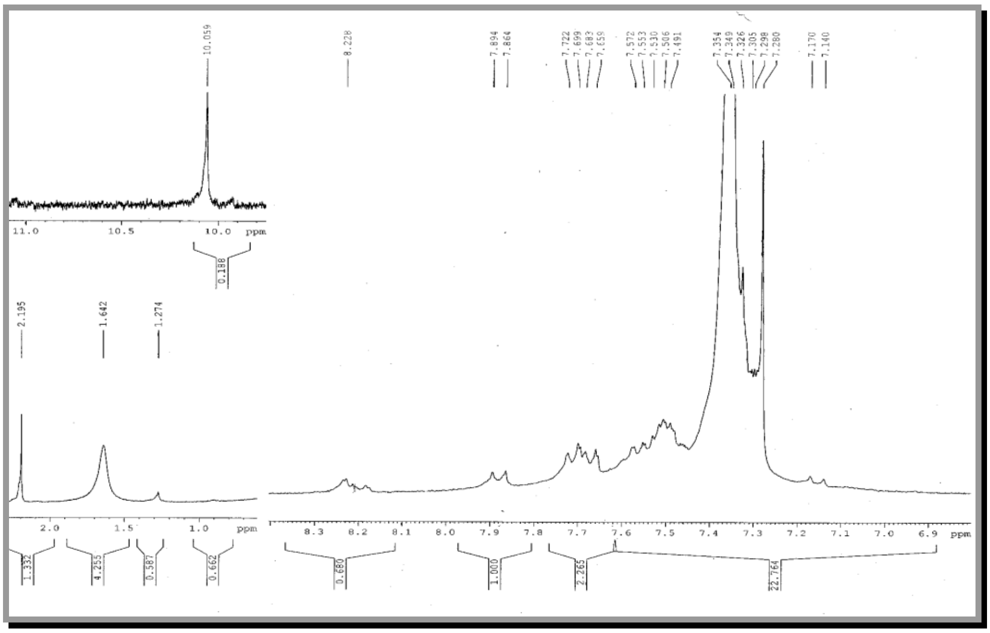

Fig. 5: ^{1}H-NMR spectrum of (CDHBDMN) L1

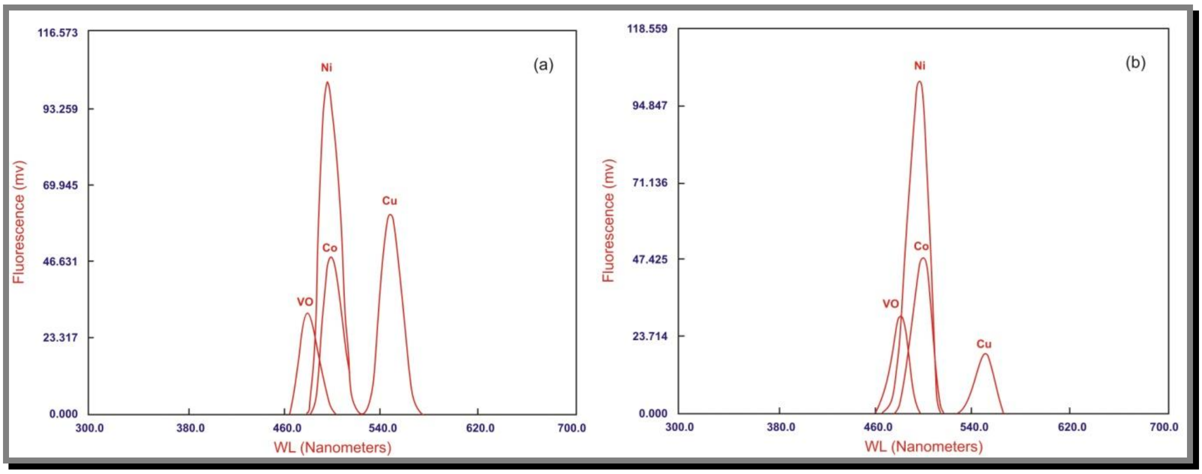

Fig. 6. a) Emission and b) Excitation spectra of metal(II) complexes

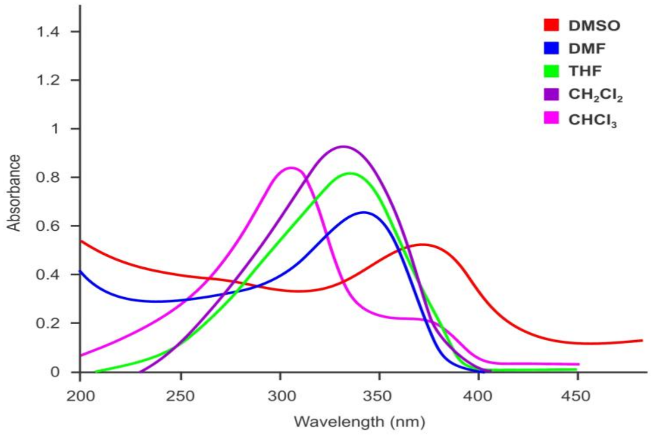

Fig. 7. Absorption spectra of Ligand 2 in various organic solvents

Table 1. Physical characterization, analytical and molar conductance data of the Ligand L1 & its complexes

Compound	FW g/mol^{-1}	Color	Found (Calcd) (%)				m.p. (°C)	Λ_M (Ω^{-1} cm^2 mol^{-1})
			M	**C**	**H**	**N**		
$C_{30}H_{18}Cl_2N_8O_2$ (CDHBDMN) **(L_2)**	592	Bright Brown	-	60.74 (60.72)	3.05 (3.06)	18.87 (18.88)	229-231	-
[VO(CDHBDMN)] **($L_2$1)**	657	Green	7.76 (7.74)	54.74 (54.73)	2.44 (2.45)	17.01 (17.02)	276-278	9.0
[Mn(CDHBDMN)] **($L_2$2)**	645	Brown	8.52 (8.50)	55.73 (55.75)	2.53 (2.50)	17.33 (17.34)	289-291	10.3
[Co(CDHBDMN)] **($L_2$3)**	649	Dark Blue	9.08 (9.06)	55.43 (55.41)	2.47 (2.48)	17.24 (17.23)	301-303	9.5
[Ni(CDHBDMN). $2H_2O$] **($L_2$4)**	684	Brownish Red	8.52 (8.55)	52.52 (52.51)	2.95 (2.94)	16.31 (16.33)	298-300	7.9
[Cu(CDHBDMN)] **($L_2$5)**	653	Dark Green	9.72 (9.70)	55.03 (55.01)	2.44 (2.46)	17.12 (17.11)	311-313	7.4
[Zn(CDHBDMN)] **($L_2$6)**	654	Brown	9.95 (9.96)	54.87 (54.86)	2.47 (2.46)	17.04 (17.06)	302-304	6.2

Table -2 Physical characterization, analytical and molar conductance data of the ligand L_2 and its complexes

Compound	Formula weight (g mol^{-1})	Colour	Found (Calcd) (%)				m.p. °C	Λ_M (Ω^{-1} cm^2 mol^{-1})
			M	**C**	**H**	**N**		
[$C_{20}H_{15}N_4O_3Cl$] (CDHBHZ) **(L_4)**	394	Bright Yellow	-	60.82 (60.84)	3.84 (3.83)	14.20 (14.19)	286-288	-
[VO(CDHBHZ).H_2O] **($L_4$1)**	477	Dark Green	10.63 (10.66)	50.29 (50.28)	3.19 (3.16)	11.75 (11.73)	>360	10.4
[Mn(CDHBHZ).H_2O] **($L_4$2)**	465	Brown	11.78 (11.80)	51.59 (51.58)	3.23 (3.25)	12.01 (12.03)	>360	10.9

[Co(CDHBHZ).H_2O] **(L$_4$3)**	469	Brown	12.58 (12.55)	51.17 (51.14)	3.23 (3.22)	11.90 (11.93)	>360	10.8
[Ni(CDHBHZ).H_2O] **(L$_4$4)**	468	Brick Red	12.49 (12.50)	51.18 (51.16)	3.25 (3.22)	11.95 (11.93)	>360	9.5
[Cu(CDHBHZ).H_2O] **(L$_4$5)**	473	Brown	13.43 (13.40)	50.65 (50.64)	3.20 (3.19)	11.79 (11.81)	>360	8.9
[Zn(CDHBHZ).H_2O] **(L$_4$6)**	474	Yellow	13.72 (13.74)	51.47 (50.44)	3.19 (3.17)	11.78 (11.76)	>360	10.2

Table 3 IR spectral data (cm^{-1}) of (CDHBDMN L1) and its metal(II) complexes

Compound	**ν (C≡N)**	**ν (CH=N)**	**ν (C-O)**	**ν (N=N)**	**ν (M-O)**	**ν (M-N)**
(CDHBDMN) **(L$_1$)**	2242	1631	1282	1402	-	-
[VO(CDHBDMN)] **(L$_1$1)**	2233	1611	1317	1401	530	485
[Mn(CDHBDMN)] **(L$_1$2)**	2240	1620	1315	1403	510	473
[Co(CDHBDMN)] **(L$_1$3)**	2237	1602	1303	1400	542	493
[Ni(CDHBDMN). 2H_2O] **(L$_1$4)**	2239	1610	1320	1402	516	480
[Cu(CDHBDMN)] **(L$_1$5)**	2241	1606	1309	1401	515	478
[Zn(CDHBDMN)] **(L$_1$6)**	2240	1604	1330	1400	540	495

Table 4 IR spectral data (cm^{-1}) of Ligand-2 and its metal(II) complexes

Compound	**ν (N-H)**	**ν (CH=N)**	**ν (C=O)**	**ν (N=C-O)**	**ν (N=N)**	**ν (M-O)**	**ν (M-N)**
(CDHBHZ) **(L$_2$)**	3200	1620	1693	-	1489	-	-
[VO(CDHBHZ).H_2O] **(L$_2$1)**	-	1610	-	1526	1490	516	480
[Mn(CDHBHZ).H_2O] **(L$_2$2)**	-	1590	-	1519	1489	521	429
[Co(CDHBHZ).H_2O] **(L$_2$3)**	-	1594	-	1506	1488	526	426
[Ni(CDHBHZ).H_2O] **(L$_2$4)**	-	1609	-	1517	1488	511	431
[Cu(CDHBHZ).H_2O] **(L$_2$5)**	-	1602	-	1525	1489	520	422
[Zn (CDHBHZ).H_2O] **(L$_2$6)**	-	1589	-	1511	1490	516	425

V. CONCLUSION

Azo Schiff base compounds have been designed and synthesized with an aim of developing NLO material. The coordination ability of the newly synthesized compounds have been proved in complexation reaction with VO(II), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) ions. Electron-drawing group in the azo-azomethine component resulted in the bathochromic effect in studied solvents. On excitation, the ligand and complexes exhibited fluorescence property which exhibit potential applications as photoactive materials. The presence of electron-pull and push substituents on the benzene ring with extended conjugation proves the compound to be a NLO material. Hence the synthesized azo Schiff base compounds might have potential application for high density optical recording media and have dye character because of their high intense color and absorption properties.

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