

Non-Linear Optical and DNA Studies of Nanostructured Schiff base Metal Complexes

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Abstract— 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 and other physical properties. The field of NLO and photonics are rapidly emerging as the technology for the 21st century. A series of potential nonlinear optical (NLO) compounds, (–OH) and (–Cl) substituted derivatives of salicylaldehyde-based ligands were designed and synthesized. The calculation results reveal that the substituent positions play a significant role in NLO properties of these compounds. The synthesized complexes are characterized by magnetic susceptibility measurements, molar conductance, elemental analysis and spectral analysis (IR, UV-Vis, ¹H-NMR, EPR and EI-mass). Metal complex mediated cleavage of DNA is a subject of continued interest, particularly toward development of new metallo-pharmaceuticals. Hence, the nuclease activity of the synthesized metal(II) complexes are studied and the result shows that the complexes cleave DNA. 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: Optical properties, DNA study, metal complexes

I. INTRODUCTION

This Coordination chemistry from the time of its inception has been a fascinating area in chemistry. During its 117 years of fundamental articles by Werner “On the structure of inorganic compounds” transformed itself from a minor section of inorganic chemistry into a vast interdisciplinary chemistry, covering a wide range of important scientific problems. The discovery of azo compounds occurred around the year 1858, which parallels the beginning of what is considered the starting point of modern organic chemistry. 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 [1-3]. Azo compounds, having conjugated electronic structures and containing substituents on the aromatic rings with push-pull electron ability [4,5] 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 [6,7]. The sequential reversible photo and thermal isomerization reactions from anti-syn-anti leads to the possibility of optical storage, photo induced switching [8, 9] and formation of surface gratings [10, 11].

The interest of the bioinorganic community in the field of metal/nucleic acid interactions has burgeoned in the last decade. This interest and the resulting progress have come about primarily because of the tremendous advances that have occurred in nucleic acid technology. Transition metal complexes that are capable of cleaving DNA under physiological conditions are of interest in the development of metal-based anticancer agents [12, 13]. Deoxyribonucleic acid (DNA) plays a significant role in the life process, because it carries the inheritance information and leads the biological synthesis of proteins and enzymes through the replication and transcription of genetic information in living cells. DNA is especially a good target for metal complexes as it gives a wide variety of potential metal binding sites [14-16].

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

ligand was determined by the modified version of powder technique in IISc, Bangalore. XRD of copper complex was recorded using OCPL/ARD/26. SEM images were recorded in a Hitachi SEM analyzer.

A. Synthesis of ligands

Ligand-1: The diazonium salt, 5-((4-chlorophenyl)diazenyl)-2-hydroxybenzaldehyde [17] (2.60 g, 0.01 mol) in ethanol was condensed by refluxing with an ethanolic solution of (1-phenyl-2,3-dimethyl-4-aminopyrazol-5-one) (2.03 g, 0.01 mol) for 3 h. The solution was allowed to stand at room temperature and the solid obtained was washed with ethanol and recrystallized [Fig. 1].

Ligand-2: 3-Formylchromone (4-oxo-4H-chromene-3-carboxaldehyde) was prepared by the Vilsmeier-Haack synthesis [18]. A mixture of 4-oxo-4H-chromene-3-carboxaldehyde (0.87 g, 5 mmol) and 1,4-phenylenediamine (0.54g, 5 mmol) in dry benzene (50 ml) containing 4-toluenesulfonic acid (0.01 g) was refluxed for 5 h. The obtained solid was filtered off and crystallized to give 3-[(4-Aminophenylimino)methyl]-4-oxo-4H-chromene [A]. Yield 78%, m.p. 201°C. Schiff base ligand 3-(4-5-(4-chlorophenyl)diazenyl)-2-hydroxybenzylideneamino)phenylimino)methyl)-4H-chromen-4-one [CDHBPC] was prepared by refluxing the precursor ligand 3-[(4-Aminophenylimino)methyl]-4-oxo-4H-chromene (1.32g, 5 mmol) [A] with 5-(4-Chlorophenylazo)-2-hydroxy-benzaldehyde (1.3g, 5 mmol) [18] for 5 h in ethanol medium. The red orange colour solid obtained was separated out and recrystallized. Yield 70%. m.p. 297° C. [Fig 2].

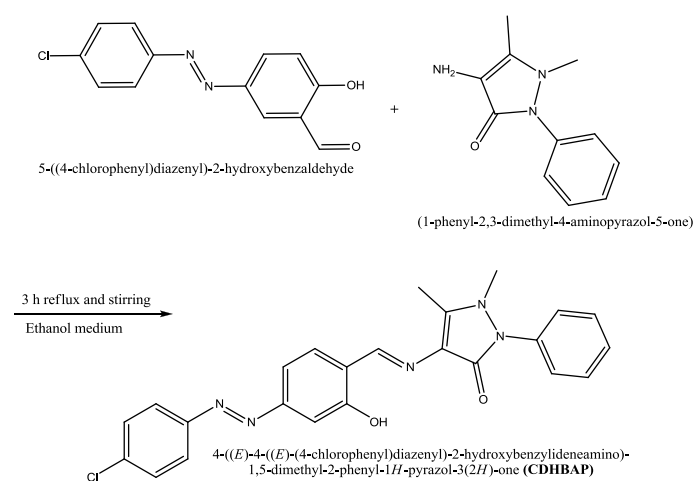


Fig. 1. Synthesis of Ligand 1 (L₁)

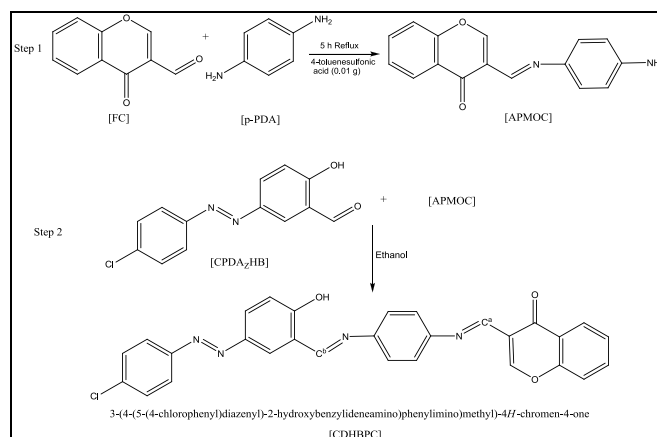


Fig. 2: Synthesis of Ligand 2 (L₂)

B. Synthesis of metal(II) complexes

A solution of metal(II) chloride/sulphate (NiCl₂·6H₂O, CuCl₂·2H₂O, ZnCl₂·2H₂O) in ethanol (1 mmol) was stirred with an ethanolic solution of L₁ and L₂ (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].

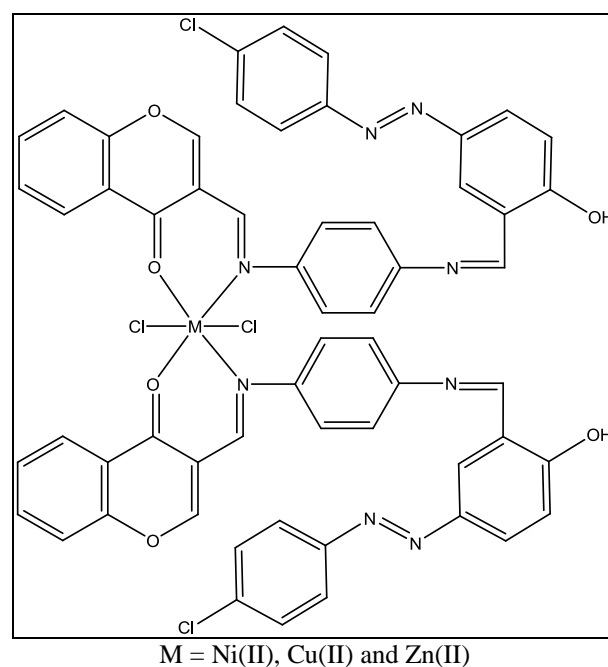


Fig 3. Proposed structure of metal(II) complexes of L₂

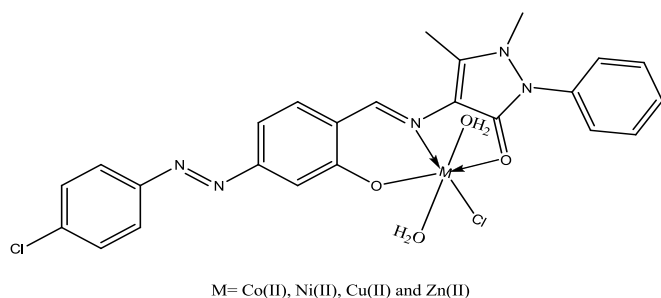


Fig. 4. Proposed structure of metal(II) complexes of L₁

III RESULTS AND DISCUSSION

The analytical data and physical properties of novel Schiff base Ligands L₁ and L₂ and their metal(II) complexes are in good agreement with calculated values (Table 1). The molar conductance of the complexes implies that the complexes are non-electrolytes. The analytical data of the complexes are consistent with the general formula [MLCl (H₂O)₂], for L₁, where M = Ni(II), Cu(II) and Zn(II) and ML₂Cl₂ type for Ni(II), Cu(II) and Zn(II) complexes of L₂.

A. IR spectra

Ligand-1: The strong band at 1640 cm⁻¹ in spectrum of the ligand is assigned to $\nu(\text{C}=\text{O})$ of the antipyrine [19]. A considerable shift (~11-40cm⁻¹) of the carbonyl frequency in complexes indicates coordination through carbonyl oxygen [20]. The ligand exhibit a strong band at 1569 cm⁻¹ assignable to $\nu(\text{C}=\text{N})$ is shifted to lower frequency (~21-46 cm⁻¹) in the spectra of the respective complexes, suggesting the coordination of the azomethine nitrogen to the metal center [21]. The $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ were identified at 507 - 541 cm⁻¹ and 400-450 cm⁻¹ [22]. A medium intensity broad band at 2933 cm⁻¹ in the spectra of free ligand is due to $\nu(\text{OH})$ stretching vibration [23]. The band at 1270 cm⁻¹ is characteristic for phenolic $\nu(\text{C}-\text{O})$ and the same is shifted to 1263-1233 cm⁻¹ in all the complexes, confirms the chelation of phenolic oxygen to metal. The existence of the broad band in the region 3438 - 3452 cm⁻¹ in all the complexes confirms the O-H stretching of the coordinated water molecules.

Ligand-2: The IR spectrum of the ligand L₂ showed characteristic bands at 3056, 1612, 1596, 1520, and 1280 cm⁻¹, assignable to $\nu(\text{OH})$, $\nu(\text{C}=\text{O})$, $\nu(\text{C}^{\text{a}}=\text{N})$ (azomethine), $\nu(\text{C}^{\text{b}}=\text{N})$ (aryl azomethine) and $\nu(\text{C}-\text{O})$ (phenolic) stretching modes, respectively [24]. In the complexes, the band due to phenolic -OH vibrations in the 3050-3075 cm⁻¹ region, remained unaltered; suggesting the non-involvement of the phenolic proton in the complex formation, and this is further supported by the $\nu(\text{C}-\text{O})$ vibrations without any change. On complexation, the $\nu(\text{C}^{\text{a}}=\text{N})$ band is shifted to lower wave numbers (1514-1489 cm⁻¹) with respect to the free ligand, suggesting that the nitrogen of the azomethine group is

coordinated to the metal ion. The non involvement of the aryl azomethine in complex formation is observed by the absence of any change in the $\nu(\text{C}^{\text{b}}=\text{N})$ vibration.

B. ¹H NMR spectra

The ¹H NMR spectrum of L₁ in deuterated DMSO shows signals consistent with the proposed structure. The multiplets around 7.0 - 7.8 ppm are assigned to aromatic protons, -C-CH₃ appears at 2.4 ppm, -N-CH₃ at 3.2 ppm, -C-CH=N- proton at 8.4 ppm. However, a singlet at 14 ppm may be attributed to the phenolic -OH of the Schiff base. The absence of this peak in the zinc(II) complex confirms deprotonation on complexation. The azomethine proton signal in the spectrum of the zinc(II) complex is shifted downfield compared to the free ligand, suggesting deshielding of the azomethine group due to coordination with metal ion.

The ¹H NMR spectrum of L₂ recorded in DMSO has the following signals confirming the structure of the ligand: 10.3 ppm (H, s, OH); 8.3 ppm (H, s, -HC^a=N-azomethine proton); 8.8 ppm (H, s, -HC^b=N-azomethine proton); 6.17-7.90 (m, aromatic protons); The ¹H NMR spectrum of zinc(II) complex in DMSO shows the presence of OH proton signal indicating the non involvement of the hydroxyl group in complexation to the metal. However, the resonance signals obtained for azomethine proton (-HC^a=N-) shifted to downfield as compared to the proton NMR of azo Schiff base suggesting the coordination of the azomethine nitrogen to Zn(II) ion.

C. Electronic spectra and magnetic moment

Electronic absorption spectral data of L₁ and L₂ and its complexes are given in Table 2. L₁ exhibits an absorption band at 29,069 cm⁻¹ due to charge transfer. The nickel(II) complex(3) exhibits three d-d bands at 13,175, 15,360, 23,866 cm⁻¹ due to ³A_{2g}(F) → ³T_{2g}(F), ³A_{2g}(F) → ³T_{1g}(F), ³A_{2g}(F) → ³T_{1g}(P) transitions arises from an octahedral geometry [32] and the same is confirmed by its magnetic moment value 2.94 B.M. The copper(II) complex(4) shows three bands, which are assigned as an intraligand charge-transfer band (28,089 cm⁻¹), ligand - metal charge transfer band (23,809 cm⁻¹) and a d-d band (15,313 cm⁻¹) may due to ²E_g → ²T_{2g} transition which strongly favors an octahedral geometry around the metal ion [25, 26] and the magnetic moment value 1.84 B.M. obtained is the normal range for octahedral symmetry. The Zn(II) complex is diamagnetic and according to the empirical formula, an octahedral geometry is proposed for this complex.

The electronic spectra of L₂ was recorded in DMSO and the Cu(II) complex shows absorption at 13,698, 15,250

Table 1. Physical characterization, analytical and molar conductance data of the ligands (L₁ and L₂) and its metal(II) complexes.

Compound	Experimental (Calcd.) (%)							
	Formula weight (g mol ⁻¹)	M	C	H	N	Yield %	m.p. °C	Λ_M (S cm ² mol ⁻¹)
[C ₂₄ H ₂₀ N ₅ O ₂ Cl](L ₁)	445.13	-	64.60 (64.65)	4.46 (4.52)	15.70 (15.71)	89	310	-
[L ₁ NiCl ₂] (3)	573.05	10.19 (10.21)	50.17 (50.13)	4.04 (4.03)	12.21 (12.18)	88	>360	8.5
[L ₁ CuCl ₂] (4)	578.04	10.92 (10.96)	47.68 (49.71)	4.01 (4.00)	12.06 (12.08)	83	>360	9.0
[L ₁ ZnCl ₂] (5)	579.04	11.20 (11.24)	49.52 (49.55)	4.00 (3.98)	12.07 (12.04)	81	>360	10.9
[C ₂₉ H ₂₁ ClN ₄ O ₃](L ₂)	506.11	-	68.70 (68.71)	3.75 (3.78)	11.02 (11.05)	75	297	-
[Ni(L ₂) ₂ Cl ₂]	1140.10	5.12 (5.13)	60.95 (60.92)	3.37 (3.35)	9.79 (9.80)	68	>360	11.0
[Cu(L ₂) ₂ Cl ₂]	1145.10	5.52 (5.53)	60.62 (60.66)	3.31 (3.34)	9.75 (9.76)	84	>360	12.4
Zn(L ₂) ₂ Cl ₂	1146.10	5.67 (5.69)	60.58 (60.57)	3.31 (3.33)	9.77 (9.74)	82	>360	10.2

Table 2. Electronic spectral data of metal(II) complexes

Compou	$\lambda_{max}(cm^{-1})$	Transition	Geometry	μ_{eff} (B.M.)
[L ₁ NiCl ₂]	13,175 15,360 23,866	³ A _{2g} (F)→ ³ T _{2g} (F) ³ A _{2g} (F)→ ³ T _{1g} (F) ³ A _{2g} (F)→ ³ T _{1g} (P)	Octahedral	2.94
[L ₁ CuCl ₂]	28,089 23,809 15,313	LMCT LMCT ² E _g → ² T _{2g}	Octahedral	1.84

and 24,325 cm⁻¹, which may be assigned to ²B_{1g} → ²A_{1g} (d_{x²-y²} → d_{z²}) (v₁), ²B_{1g} → ²B_{2g} (d_{x²-y²} → d_{zy}) (v₂), ²B_{1g} → ²E_g (d_{x²-y²} → d_{zy}, d_{yz}) (v₃) transitions and the magnetic susceptibility value (1.93 μ_B) confirms the octahedral geometry [27]. The magnetic moment value 3.26 B.M. for Ni(II) complex as well as the electronic spectrum centered around 9690, 16332 and 23,750 cm⁻¹ assigned to ³A_{2g}(F) → ³T_{2g}(F) [v₁], ³A_{2g}(F) → ³T_{1g}(F) [v₂] and ³A_{2g}(F) → ³T_{1g}(P) [v₃] transitions, confirm

octahedral geometry around the Ni(II) ion. The Zn(II) complex is diamagnetic and an octahedral geometry for Zn(II).

D. Gel electrophoresis

The cleavage reaction was monitored by gel electrophoresis. The electrophoresis clearly revealed that, the Schiff base L₁ and their metal(II) complexes have acted on DNA as there was difference in the bands of lanes compared to the control DNA. (Fig. 5). The cleavage efficiency of the complexes compared to that of the control is due to their efficient DNA-binding ability. The metal(II) complexes are able to convert supercoiled DNA into open circular DNA. General oxidative mechanisms account for DNA cleavage by hydroxyl radicals via abstraction of a hydrogen from sugar units and predict the release of specific residues arising from transformed sugars, depending on the position from which the hydrogen is removed [28]. The reaction is modulated by a bound hydroxyl radical or a peroxy species generated from H₂O₂.

In this study, the CT-DNA gel electrophoresis experiment was conducted at 35°C using the synthesized complexes in the presence of H₂O₂ as an oxidant. From the Fig. 5, it is observed that the control DNA (lane 1) does not show any significant cleavage of CT-DNA even on longer exposure time. Ni(II) and Cu(II) complexes (lane 2 & 3) cleave DNA as compared to control DNA while other

complexes do not cleave that much in the presence of H_2O_2 . The presence of a smear in the gel diagram indicates the presence of radical cleavage [29] and the cleavage efficiency of the complexes is comparable to that of the control is due to their efficient DNA-binding ability. As the compound was observed to cleave the DNA, it can be concluded that the compound inhibits the growth of the pathogenic organism by cleaving the genome.



Lane 1= DNA alone, Lane 2 = CDHBAP,
Lane 3=DNA +Ni complex, Lane 4=DNA +Cu complex
Lane 5=DNA +Zn complex

Fig. 5. DNA study of metal(II) complexes

E. Nonlinear optical properties of ligand

Nonlinear optics (NLO) properties of organic and inorganic molecules have been the subject of extensive theoretical and experimental investigations during the last two decades. Total first hyperpolarisability (β_{tot}) for Schiff base ligand is studied here and Schiff base shows the better second harmonic efficiency than urea and KDP. The ligand L_1 is 2.1 times more active than that of urea and KDP. From the results obtained one may conclude that organic NLO molecules, the azo Schiff base especially that derived from the reaction of salicylaldehyde with amines have attracted interest because of their relative delocalization of the π -electronic clouds. Hence the donor- (π -electron bridge)-acceptor (D- π -A) structures, as a simple molecular model, have been successfully used in the development of second-order NLO compounds [30]. The novel Azo Schiff base ligand L_2 show 2.7 and 3.2 times more activity than urea and KDP respectively. Ligand has donor-acceptor property and the electron-withdrawing atom of chlorine can prevent the lone pair electron of nitrogen atom in $N=N$ group to be delocalized and causes a reduction in second-order nonlinearity [31].

F. Scanning electron microscopy (SEM)

Scanning electron microscopy is used here to evaluate morphology and particle size of the azo Schiff base metal complexes. From the SEM image of Cu(II) complex of L_1 (Fig. 6), a single phase formation having layer by layer like morphologies with particle size $1 \mu m$ is observed. In general, the SEM photograph show single phase formation with well-defined grain like shape and particle size in the range of $1 \mu m$.

The morphology and particle size of the Schiff base Cu(II) complex of L_2 have been illustrated by the scanning electron microscopy (SEM). Fig. 7 depicts the SEM photograph of the synthesised Cu(II) complex. We noted that there is a uniform matrix of the synthesized complex in the pictograph. This leads us to believe that we are dealing with homogeneous phase material. The image of the copper complex depicted in Fig.7 presents the growth of both vertically and horizontally aligned blocks with irregularity and density and confirms the presences of compounds with the particle size of $2 \mu m$.

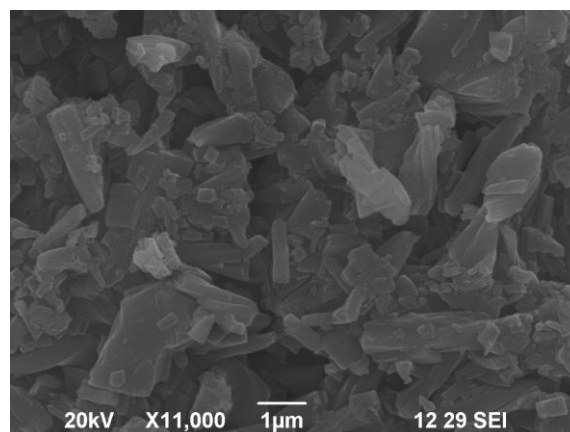


Fig. 6. SEM image of Cu(II) complex of L_1

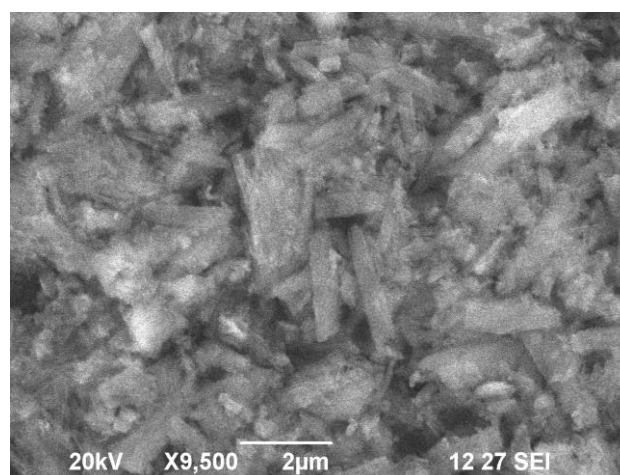


Fig. 7. SEM image of Cu(II) complex of L_2

G. X-ray diffraction study

Crystals suitable for X-ray analysis (Fig. 8) was obtained by slow evaporation of an ethanolic solution of the azo Schiff base ligand CDHBAP and yielded orange blocks after 7 days. X-ray diffraction data were collected on a Bruker APEX 2 CCD platform diffractometer equipped with an Oxford liquid nitrogen cryostream. Crystals were mounted in a nylon loop with Paratone-N cryoprotectant oil. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F² with SHELXTL (Version 6.14)

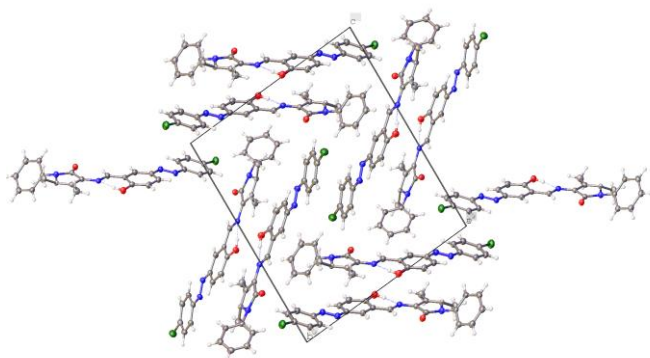


Fig. 8. Crystal structure of the Schiff base ligand [L₁]

CONCLUSION

On the basis of various physico-chemical and spectral data presented and discussed above, the complexes of L₁ may tentatively be suggested to have octahedral geometry. The interaction of these complexes with CT-DNA was investigated by gel electrophoresis and concluded that Cu(II) complex cleave DNA in the presence of H₂O₂, whereas the control DNA, CDHBAP and other complexes are not effective.

The Schiff base complexes of Ni(II), Cu(II) and Zn(II) derived from L₂ were synthesized and characterized on the basis of analytical and spectral data. The results of this investigation support the suggested octahedral structure of the metal complexes and form a favorable molecular arrangement so that the material show relatively strong solid state NLO properties with the relative SHG efficiency of the material 2.7 and 3.2 times more active than urea and KDP. Presence of two azomethine and a more extended conjugated system shows higher luminescence efficiency of the synthesized compounds. All the compounds are thermally very stable with high melting point and intense color and are attractive from the point of view of studying photoinduced effects in theoretical and experimental areas.

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