

SYNTHESIS AND CHARACTERIZATION OF ZN(II) AND Cd(II)

SALEN COMPLEXES , SALEN L1H2 , L2H2 N,N'-BIS

(SALICYLIDENE)-8,11 DIAMINOCTANE AND N,N'-BIS

(SALICYLIDENE)-8,13 DIAMINODECANE

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ABSTRACT

We describe the synthesis and characterization of two salens L1H2 , L2H2 ligands and four Zn(II) and Cd(II) complexes of the tetradentate salens ligands N,N'-bis (salicylidene)-8,11 diaminoctane and N,N'-bis (salicylidene)-8,13 diaminodecane. The complexes ML1 and ML2 M=Zn²⁺, Cd²⁺ were synthesized by treating an ethanolic solution of the ligand salen with equimolar amounts of metal chloride and two equivalent with potassium hydroxide. The L1H2,L2H2, and the ML1,ML2, M=Zn²⁺, Cd²⁺ complexes were characterized by molar conductivity, FTIR ,¹H,¹³C, NMR, UV-Visible. According to obtained data ,the probable coordination geometries of Zinc(II) and Cadmium(II) in these complexes are tetrahedral.

Keywords: Salens, diaminoctane, diaminodecane, Zn(II) , Cd(II), UV-visible, ¹H ,¹³C ,NMR.

INTRODUCTION

The coordination chemistry of Schiff bases and especially the salen ligand (salenH₂) tetradentate and pentadentate is highly developed^{1,2}, most research has involved the skeleton of the aromatic ligand salenH₂ and this for different substituent (position, nature, etc...) . On the aromatic ring in order to modulate the stereochemistry and physical-chemical properties of the ligand and complexes based on the properties of the metal cation. Most of the series of cations of transition elements form stable complexes with these ligands salenH₂. Salens complexes have raised many fundamental studies and applied in several fields of medicine³, chemistry and physics^{4,5}.

MATERIALS AND METHODS

All reagents were purchased commercially and used without further purification, salicylaldehyde was purchased from FULKA , the zinc chloride (ZnCl₂, 2H₂O) and cadmium chloride (CdCl₂, 1/2H₂O) were obtained from Panreac, Ethanol and DMF Sigma Aldrich.

The ¹H, ¹³C NMR spectra were recorded with a

Bruker AVANCE 300. Infrared spectra were recorded on JASCO FTIR660 spectrophotometer in range of 4000-400 cm⁻¹. The UV-Visible spectra were recorded on Shimadzu UV-1800 Spectrophotometer. The conductivity measurements were performed at 25°C in DMSO using Hach HQ430d flexi.

Synthesis of ligands L1H2 and L2H2

The salen ligand N,N'-bis (salicylidene)-8,11 diaminoctane L1H2 and N,N'-bis(salicylidene)-8,13 diaminodecane L2H2 were synthesized by condensation of the salicylaldehyde and appropriate diamines in 2 : 1 molar ratio by refluxing in distilled ethanol. The yellow precipitate was filtered, washed with ethanol.

Preparation of complexes

A mixture of L1H2 or L2H2 (0.5mmol) and (ZnCl₂, 2H₂O) or (CdCl₂, 1/2H₂O) (0.5mmol) in absolute ethanol (20ml) and potassium hydroxide KOH (1mmol), the resulting mixture was refluxed for (3-4) hours.

The precipitate obtained was filtered, washed with aqueous ethanol followed by distilled water and dried.

Yield: 0.5mmol (60-70)% , MP ZnL8 226°C ,ZnL10 230°C ,CdL8 >260°C,CdL10>260°C.

RESULTS AND DISCUSSIONS

The prepared complexes were found to be solids , insoluble in water but they were soluble in some organic solvents like DMF and DMSO. The molar conductance of the complexes measured for 10-4 M solution in DMSO or DMF at room temperature, indicates the non electrolytic nature⁶.

¹H,¹³C NMR Spectroscopy of salens L₁H₂ , L₂H₂ and the salens complexes ML₁, ML₂ , M=Zn²⁺, Cd²⁺

The ¹H,¹³C NMR spectral studies of salens L₁H₂ and L₂H₂ and their salen complexes of Zn(II) and Cd(II) have been recorded in CDCl₃ at room temperature.

¹H NMR spectra of salens L₁H₂ and L₂H₂, show a broad singlet around 13.73 ppm and 13.75 ppm corresponding to the phenolic proton⁷, and also a singlet at 8.34 ppm characteristic of azomethine hydrogen of CH =N group⁸.

The multiplets corresponding to phenyl protons for salens L₁H₂ and L₂H₂ appear in the range (6.98-7.2) ppm⁸. ¹H NMR spectrum of L₁H₂ is given in the Figure (2).

The presence of a triplet dedoublet at 3.60 ppm for the methylene indicates, the nonequivalent nature of methylene C8 protons N—H₂C (8) . The spectra of L₁H₂ and L₂H₂ contain two triplets at δ=(1.73,1.70) ppm and multiplet at

δ=(1.35,1.41) ppm can be assigned to methylene N—H₂C(9) and N—H₂C(10,11) or N—H₂C(10,12) protons of long methylene chain Table(1).

In ¹HNMR spectra of the complexes we observed an electron density shift from the ligand to the metal. The signals of the azomethine protons appear deshielded at 8.52 and 8.43 ppm in the Zinc complexes as compared to 8.34 ppm in the L₁H₂ and L₂H₂ salens free, in fering coordination though the azomethine nitrogen atom of the salens (L₁H₂ , L₂H₂).

Disappearance of the singlet phenolic OH proton in the spectra of the complexes ML₁, ML₂ supported the deprotonation of the phenolic group^{9,10}. Figure (3;4).

All ¹HNMR data are summarized in Table (1). The molecular structure of L₁H₂ and L₂H₂ Figure (1) was further verified by using ¹³CNMR spectroscopy Figure (3;4). A peaks at δ=(26.82-30.82) ppm is contributed by the methylene carbons of long chain, a peak at δ=(58.55-59.50) ppm is attributed to the carbon N—H₂C(8)¹¹. The peak at δ=(161-116) ppm is assigned to six aromatic carbons. The most downfield peak in the spectrum δ=164.45ppm (L₂H₂),is ascribed to carbon C1 azomethine group.

The ¹H,¹³C NMR spectral of all the complexes showed a downfield shift in the frequency of azomethine C(1)H= N, —N—H₂C(8) — , at (172.3-166.12) ppm and (60.05-59.54) ppm for ZnL₂ confirming coordination of the metal ion¹² Table (2).

All ¹³CNMR data are summarized in Table (2).

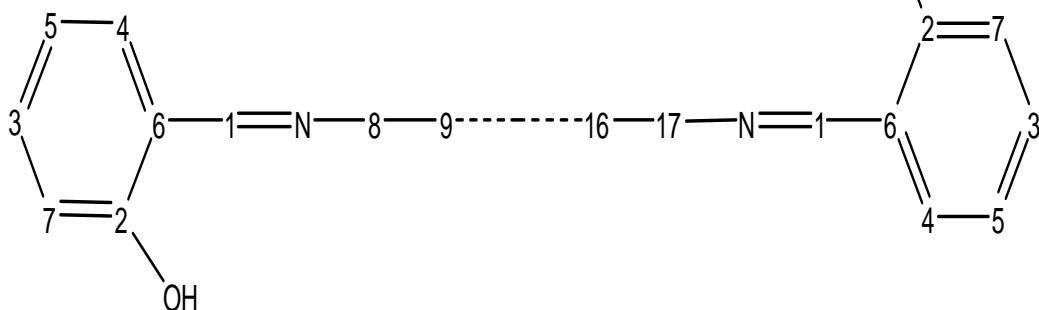


Fig. 1: Structures of salen ligand L₁H₂ and numbering of carbons

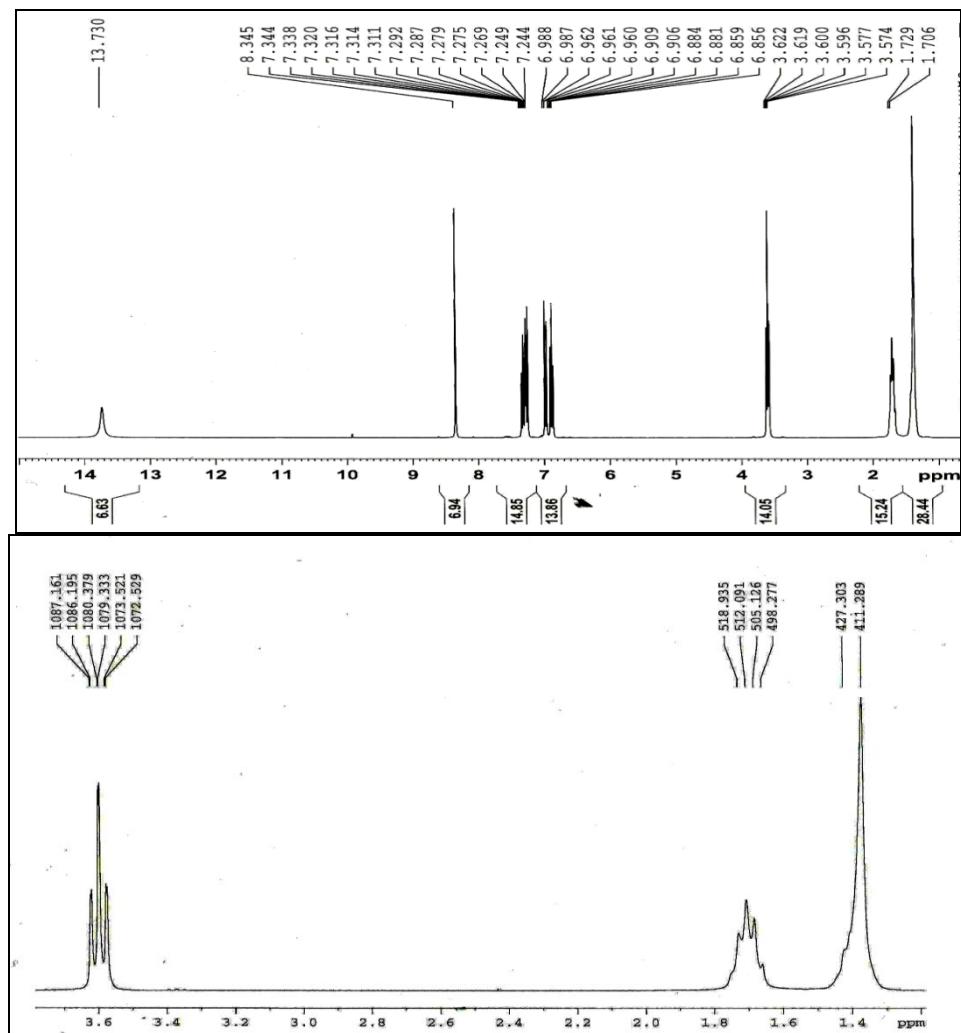


Fig. 2: ^1H NMR spectrum of salen ligands L1H2 in CDCl_3 at 300 MHz

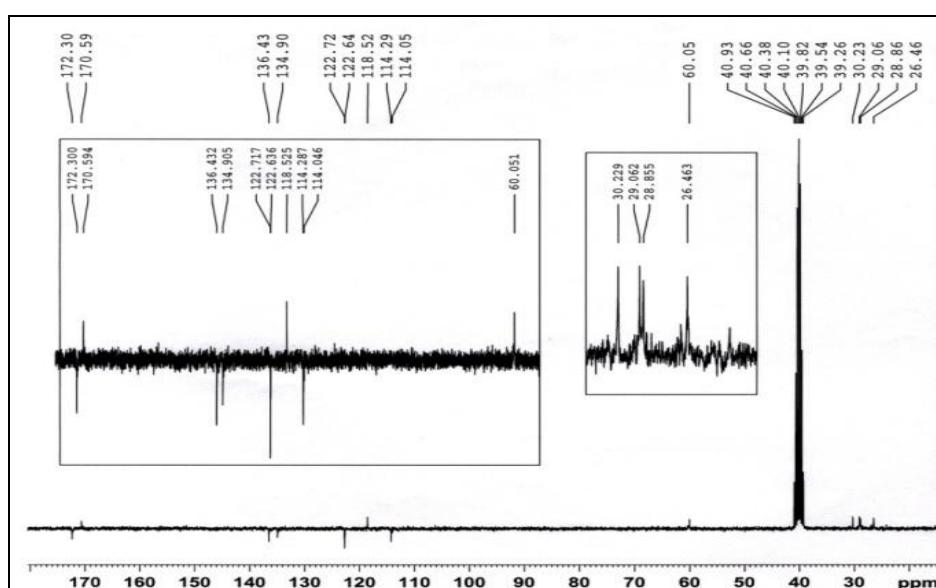
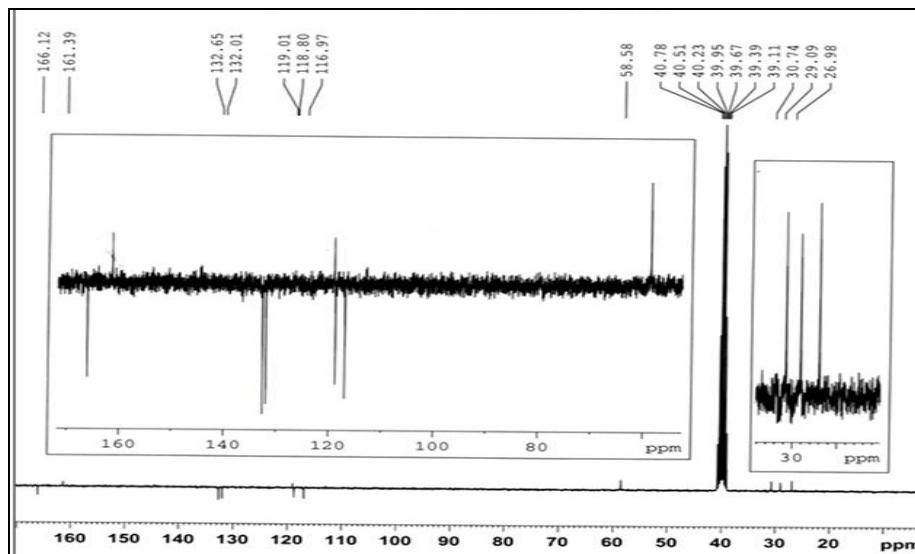


Fig. 3: ^{13}C NMR spectrum of complexes ZnL2 in CDCl_3 at 300 MHz

Fig. 4: ^{13}C NMR spectrum of complexes CdL1 in CDCl_3 at 300 MHz**Table 1:** ^1H NMR data of ligands L₁H₂, L₂H₂ and complexes ZnL₁, ZnL₂, CdL₁, CdL₂ in CDCl_3 at 300 MHz

Ligands L ₁ H ₂ , L ₂ H ₂ and complexes	δ OH	δ CH=N	δ Sal H	δ N(CH ₂)n
L ₁ H ₂	13.73(2,1H.s)	8.34(1,1H.s)	7.2-6.98(4H,m) 6.85 (4H,m)	3.60(8,2H,tt) 1.73(9,2H,tt)J=6.85,J=6.97 1.35(10,11,4H,ttt)
L ₂ H ₂	13.75(2.1H.s)	8.34(1.1H.s)	7.2-6.9(4H,m)	3.60(8,2H,tt) 1.70(9,2H,tt)J=6.82,J=7.2 1.41(10,12,4H,m)
ZnL ₁	--	8.52 (1H)	7.28- 6.84 (4H,m)	3.24(8,2H,m) 2.5(9,2H,m) 1.24(10,11,4H,m)
ZnL ₂	--	8.43 (1H)	7.21-6.56 (4H,m)	3.26(8,2H,m) 2.49(9,2H,m) 1.27(10,12,4H,m)
CdL ₁	--	8.57 (1H)	7.33-6.85(4H,m)	3.34(8,2H,m) 2.47(9,2H,m) 1.25(10,11,4H,m)
CdL ₂	--	8.53 (1H)	7.40-6.85 (4H,m)	3.31(8,2H,m) 2.50(9,2H,m) 1.29(10,12,4H,m)

Table 2: ^{13}C NMR data of ligands L₁H₂, L₂H₂ and complexes CdL₁, CdL₂, ZnL₂, in CDCl_3 at 300 MHz

Ligands L ₁ H ₂ , L ₂ H ₂ and complexes	The chemical shifts δ (ppm)
L ₁ H ₂	164.48 C1 ; 161.4 C2 ; 132.04 C3 ; 131.08 C4 ; 118.39 C5 ; 118.82 C6 ; 117.04 C7 59.50 C8 ; 30.82 C9 ; 29.24 C10 ; 27.12 C11 .
L ₂ H ₂	164.45 C1 ; 161.43 C2 ; 132.04 C3 ; 131.08 C4 ; 118.82 C5 ; 118.38 C6; 117.05 C7 ,59.54C8; 30.86 C9 ; 29.49 C10 ; 29.33 C11 ; 27.17 C12.
CdL ₁	166.12 C1 ; 161.39 C2 ; 132.65 C3 ; 132.01 C4 ; 119.01 C5 ; 118.80 C6 ; 116.97 C7 58.58 C8 ; 30.74 C9 ; 26.98 C10 ; 29.09 C11
CdL ₂	166.10 C1 ; 161.42 C2 ; 132.66 C3 ; 132.00 C4 ; 119.00 C5 ; 118.78 C6 ; 116.98 C7 ; 58.55 C8 ; 30.74 C9 ; 29.32 C10 ; 29.07 C11 ; 26.98 C12
ZnL ₁	165.80 C1 ; 161.40 C2 ; 132.18 C3 ; 131.18 C4 ; 118.86 C5 ; 118.92 C6 ; 117.07 C7 ; 59.54 C8 ; 30.80 C9 ; 29.46 C10 ; 29.38 C11 .
ZnL ₂	172.3 C1 ; 170.59 C2 ; 136.43 C3 ; 134.9 C4 ; 118.52 C5 ; 114.29 C6 ; 114.05 C7 ; 60.05 C8 ; 30.22 C9 ; 29.06 C10 ; 28.85C11 ; 26.46 C12

Infrared Spectroscopy of salens L₁H₂, L₂H₂ and the salen complexes

The important infrared frequencies exhibited by the salen ligands L₁H₂ and L₂H₂ and their complexes are given in the Table(3;4).

The infrared spectra of L₁H₂ and L₂H₂ show also a weak band at 3044 cm⁻¹ and 3051 cm⁻¹ assigned to (ν CH, ArCH), and two broad bands^{11,20}. figure(5).

The first broad band is centered at around 3430 cm⁻¹ and 3442 cm⁻¹ due to the phenolic hydroxyl group perturbed by intramolecular hydrogen bonding (O-H.....N) respectively in free ligands¹², in the complexes, this band is associated with coordinated water molecules¹³. However the second broad band between 2655 cm⁻¹ 2302 cm⁻¹ and might be designated for internal hydrogen bond for (OH.....N=C), which disappeared in spectra of their complexes indicating probably the coordination through phenolic oxygen moiety¹⁴.

The spectra of salen ligands free containing the band which are assigned to the vibrations ν CH₂, δ CH₂ and ρ CH₂ Table(3).

The infrared spectra of the salens L₁H₂ and L₂H₂ exhibit a strong band at 1634 cm⁻¹ and 1630 cm⁻¹ due to ν C=N which has been shifted towards lower region at around (1628-1619) cm⁻¹ in the spectra of complexes indicating the coordination of the azomethine group in the complex formation^{15,16} figure(6) Table(4).

In the spectra figure(6), a medium intensity band at around 1283 cm⁻¹ and 1273 cm⁻¹ due to phenolic hydroxyl deformation vibration is shifted to lower region at (1186,1187) cm⁻¹ respectively due to the phenolic ν (C--O) indicating the coordination through the phenolic oxygen atoms Table(4).

The coordination through nitrogen of azomethine and oxygen of phenolic group of salen ligands are further evidenced by the appearance in the complexes of non-ligand band around (583,587) cm⁻¹ and (410,437) cm⁻¹ are due to M—O and M—N bonds respectively^{17,3} Table(4;5) figure(6;7).

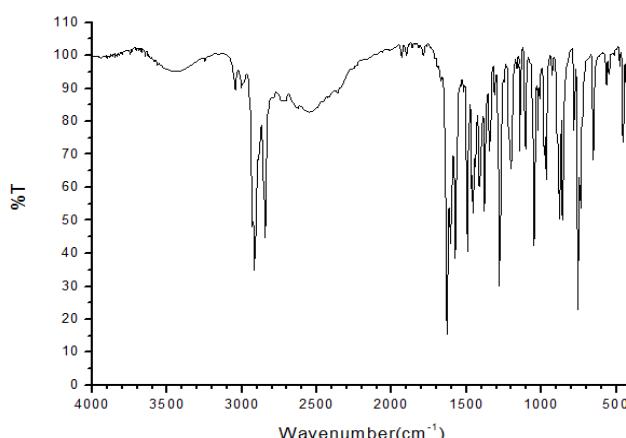


Fig. 5: Infrared spectrum of ligands L₁H₂ and L₂H₂

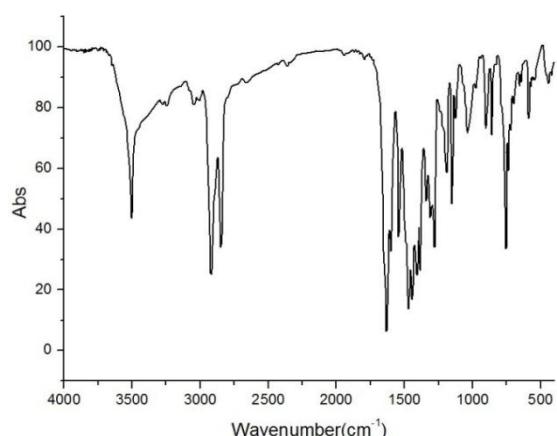
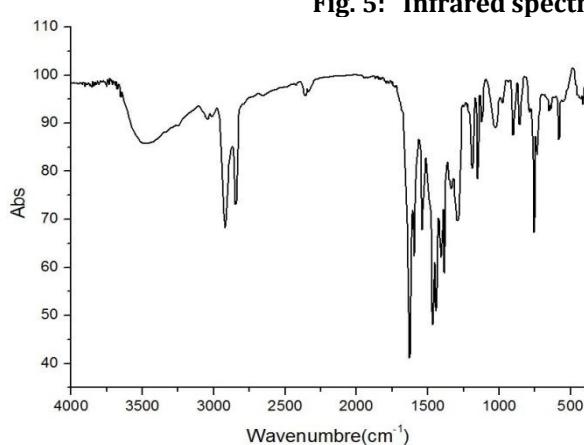
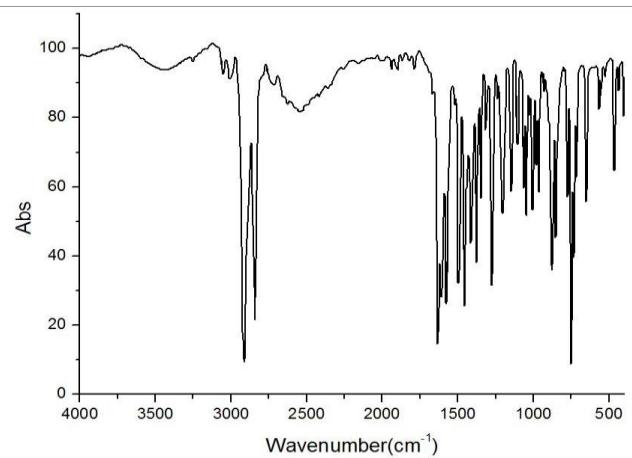
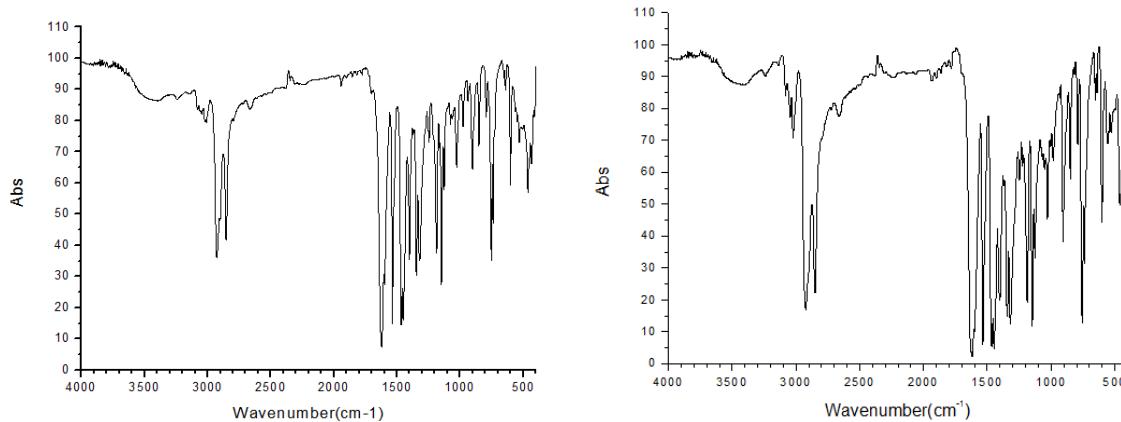


Fig. 6: Infrared spectrum spectrum of complexes Cd L1 and Cd L2

**Fig. 7: Infrared spectrum spectrum of complexes ZnL1 and ZnL2****Table 3: Infrared data of ligands L₁H₂ and L₂H₂ in the solid state in KBr**

Attribution	n=8 L ₁ H ₂	n=10 L ₂ H ₂
	Wave number (cm ⁻¹)	Wave number (cm ⁻¹)
vOH	3430(w)	3442(w)
vCH(ar)	3044(w) 3002(w)	3051(w) 3003(w)
vCH(alph)	2916(s)	2911(vs)
vCH(alph)	2845(s)	2839(s)
vC=N	1630(vs)	1634(vs)
vC=C	1575(m)	1577(m)
vC=C	1519(w)	1516(w)
vC=C	1494(m)	1495(m)
δCH ₂	1453(m)	1456(m)
δCH ₂	1412(m)	1416(m)
δCH ₂	1381(m)	1375(m)
δCH ₂	1346(w)	1347(m)
δOH	1283(s)	1273(s)
δCO	1205(m)	1203(m)
δCH	1142(w)	1145(m)
vC-C-C	1103(w)	1102(w)
δC=C-H	1049(m)	1049(w)
vC-C	1022(w)	1027(w)
vC-C	1008(w)	1004(m)
vC-C	979(w)	983(w)
vC-C	967(w)	965(w)
vC-C	878(w)	876(m)
vC-C	857(m)	855(m)
ρCH(ar)	782(w) 756(s)	776(m) 751(s), 718(w)
ρCH	651(m)	650(m)
vC-C-C	563(w) 542(w) 477(w), 453(w) 434(w), 401(w)	567(w) 555(w) 463(w) 435(w), 402(w)

Table 4: Infrared data of complexes Cd L1 and Cd L2 in the solid state in KBr

Attribution	n=8 CdL ₁	n=10 CdL ₂
	Wave number (cm ⁻¹)	Wave number (cm ⁻¹)
vOH(H ₂ O)	3480(w)	3500(w)
vCH(ar)	3013(w)-3040(w)	3010(w)-3046(w)
vCH(alph)	2922(s)	2917(s)
vCH(alph)	2846(s)	2848(s)
vC=N	1628(vs)	1625(vs)
vC=C	1593(s)	1599(s)
vC=C	1538(s)	1543(m)
δCH ₂	1467(vs)	1469(vs)
δCH ₂	1443(vs)	1442(vs)
δCH ₂	1407(s)	1407(s)
δCH ₂	1381(m)	1383(m)
δCH ₂	1335(w)	1339(m)
vCO	1186(m)	1189(m)
vC-C-C	1149(m)	1150(m)
vC-C-C	1122(w)	1124(w)
vC-C-C-H	1023(w)	1037(w)
vC-C	974(w)	975(w)
vC-C	901(w)	902(w)
vC-C	855(w)	857(w)
ρCH(ar)	791(w) 755(s) 733(w)	756(s) 736(w)
ρCH	650(w)	653(w)
vCd-O	583(m)	587(m)
vCd-N	410(w)	437(w)

Table 5: Infrared data of complexes ZnL1 and ZnL2 in the solid state in KBr

Attribution	n=8 ZnL ₁	n=10 ZnL ₂
	Wave number (cm ⁻¹)	Wave number (cm ⁻¹)
vOH(H ₂ O)	3400(w)	3405(w)
vCH(ar)	3009(w)-3046(w)	3021(w)-3044(w)
vCH(alph)	2927(s)	2922(vs)
vCH(alph)	2854(s)	2850(s)
vC=N	1621(vs)	1619(vs)
vC=C	1536(s)	1536(vs)
δCH ₂	1465(s)	1465(s)
δCH ₂	1450(s)	1448(s)
δCH ₂	1401(s)	1400(s)
δCH ₂	1346(s)	1345(s)
δCH ₂	1320(s)	1320(s)
vCO	1186(m)	1187(m)
vC-C-C	1147(s)	1147(s)
vC-C-C	1126(m)	1126(m)
vC-C-C-H	1026(w)	1028(m)
vC-C	977(w) 938(w) 902(w) 850(w)	984(w) 932(w) 906(m) 849(m)
ρCH(ar)	793(w) 751(s) 738(m)	970(w) 755(s) 737(m)
ρCH	639(w)	652(w)
vZn-O	600(m)	599(m)
vZn-N	462(m)	461(m)

UV-Visible Spectroscopy

The electronic spectra studies of salen complexes of Zn(II), Cd(II) with salens L₁H₂ and L₂H₂ were carried out in DMF solution figure(8;9).

In the electronic spectrum of the salens free are two absorption band assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition¹⁸ Table(6).

These transition are found also in the spectra of the complexes, but they are shifted towards high frequencies and new absorption band are observed in the region (398-392) nm, are assigned to charge transfer transition¹⁹.

The Cd(II) and Zn(II) complexes show only the charge transfer transition from the salen to the metal and vice versa, no d-d transition are expected for d¹⁰ complexes.

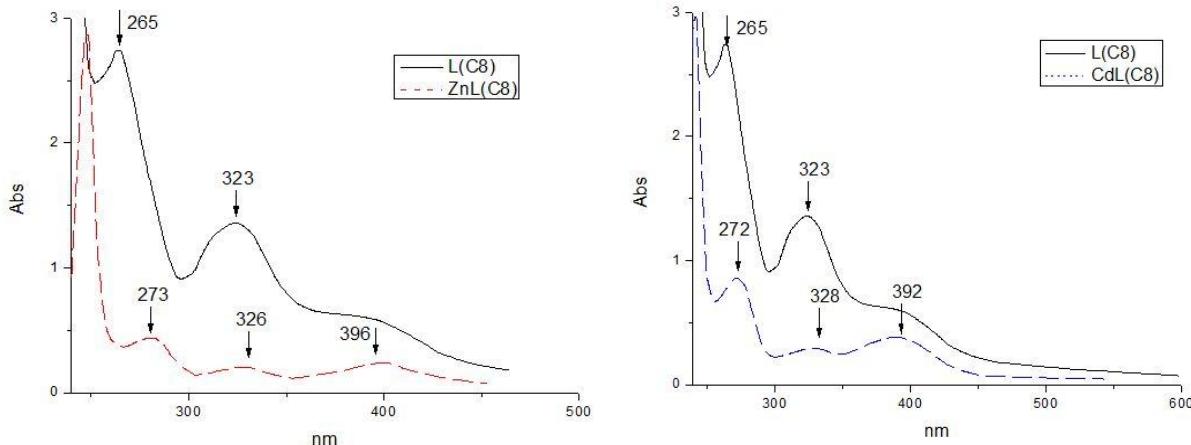


Fig. 8: UV-Visible spectrum of the ligand L1H2 and complexes ZnL1, CdL1

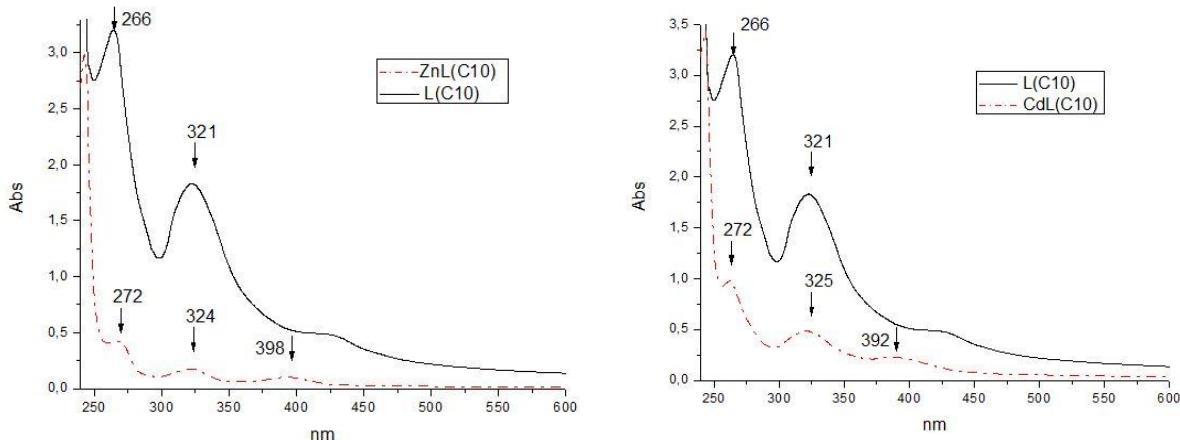


Fig. 9: UV-Visible spectrum of the ligand L2H2 and complexes ZnL2, CdL2

Table 6: UV-Visible data of ligands L1H2 ,L2H2 and complexes ZnL1, ZnL2 ,CdL1 ,CdL2

Compound	$\lambda_{\text{max}}(\text{nm})$
L ₁ H ₂	265($\pi \rightarrow \pi^*$) ; 323($n \rightarrow \pi^*$)
L ₂ H ₂	266($\pi \rightarrow \pi^*$) ; 321($n \rightarrow \pi^*$)
ZnL ₁	273($\pi \rightarrow \pi^*$) ; 326($n \rightarrow \pi^*$) ; 396(d $\rightarrow \pi^*$).
ZnL ₂	272($\pi \rightarrow \pi^*$) ; 324($n \rightarrow \pi^*$) ; 398(d $\rightarrow \pi^*$).
CdL ₁	272($\pi \rightarrow \pi^*$) ; 328($n \rightarrow \pi^*$) ; 392(d $\rightarrow \pi^*$).
CdL ₂	272($\pi \rightarrow \pi^*$) ; 325($n \rightarrow \pi^*$) ; 392(d $\rightarrow \pi^*$).

CONCLUSION

On this paper we present the results of a study of the two salens L_1H_2 , L_2H_2 derived from salicylaldehyde and diaminooctane or diaminodecane and their complexes ML_1 and ML_2 $M=Zn(II)$, $Cd(II)$. The salen ligands and the complexes were characterized by 1H , ^{13}C NMR, UV-visible and infrared spectra. L_1 , L_2 acts as a tetridentate ligands by coordination via the nitrogen atoms of azomethine groups ($CH=N-$) and oxygen atoms of phenolic hydroxy groups in an Td symmetry.

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