

Preparation and Study Of Zn(II) Complexes With Some Schiff Bases Derived From Acid Hydrazide-Benzil and Ethylenediamine

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الخلاصة

ذوات الصيغة بعض المعقدات الحلقية وغير الحلقية الجديدة $[Zn_2LCl_4]$, $[ZnLCl_2]$, $[ZnL]Cl_2$ حيث $L =$ ليكاند من نوع قاعدة شيف مشتقة من الاثيلين ثنائي الأمين مع بعض الاسترات (أثيل ثنائي مالونيت، أثيل ثنائي سكسينيت، أثيل ثنائي فتاليت) والبرزول مع كلوريد الزنك في الايثانول. حضرت المعقدات بنسبة 1:1، 1:2، 2:1 فلز-ليكاند، تم تشخيص المعقدات بطرق تحليل العناصر وقياس التوصيل الكهربائي وأطياف الأشعة تحت الحمراء وأطياف فوق البنفسجية. وقد أظهرت هذه الدراسات الليكاندات بشكل رباعي وثمانى السن لتنتج معقدات رباعية وسداسية التن اسق ذات بنية رباعي وثمانى السطوح على التوالي.

Abstract

Some new macrocyclic and acyclic complexes having the general formula $[ZnL]Cl_2$, $[ZnLCl_2]$, $[Zn_2LCl_4]$ where $L =$ Schiff base ligands derived from ethylene diamine with esters (diethylmalonate, diethylsuccinate and diethylphthalate) and benzil, where prepared by the reaction of zinc (II) chloride with ligands in ethanolic solution. 1:1, 2:1, 1:2 stoichiometry of zinc (II) to ligand. Elemental analysis, molar conductance, infrared and ultraviolet studies reveal that the ligands in these complexes behave as tetra and octadentate forming tetra and hexa coordinated zinc (II) complexes respectively.

Introduction

Schiff base molecules considered as important ligands in coordination chemistry. These ligands interested many workers and several reviews and papers appeared revealing their preparation and coordination complexes⁽¹⁻³⁾. Schiff bases are very important from many points of view. They could be present (in addition to their solid crystal forms) as liquid crystal⁽⁴⁾. In coordination chemistry, they act as ligands due to their selectivity and sensitivity to the reaction with transition and non transition metal ions^(5,6). The design and synthesis of polydentate schiff bases and their properties and potential in the selective coordination of metal ions is reviewed^(7,8). Self-condensation reaction of appropriate formyl or keto precursors with suitable polyamines can give rise to well defined planer or tridimensional macrocyclic or macroacyclic schiff bases, but different reaction path ways can also occur⁽⁹⁻¹¹⁾. Multidentate macrocyclic ligands are cyclic molecules consisting of an organic framework interspersed with hetero atoms which are capable of interacting with a variety of species⁽¹²⁾. They display unique and exciting chemistries in that they can function as receptors for substrates of widely differing physical and chemical properties and upon complexation can drastically alter these properties⁽¹³⁾. For these molecules, the nature and chemical reactivity of the resulting complexes are closely associated with the ligand at framework⁽¹⁴⁾. Considerable number of metal complexes with four and six nitrogen and oxygen donor macrocyclic ligand have been reported⁽¹⁵⁾. The biological activity of these schiff base complexes which bearing amide, azomethine and hydrazide groups is due to their action as the rapeutic agent owing to their easy hydrolysis providing low toxicity⁽¹⁶⁻¹⁸⁾. We are engaged in research including the synthesis of schiff base ligands-benzolidine ethylene diamine and their new metal complexes. The research aimed also to elucidate the active site of the ligands and the possible structure and properties of the complexes.

Experimental

All reagents and solvents were of analytical grade. The ligands benzilidene ethylene diamine were prepared by the condensation of diethyl malonate, diethyl succinate or diethyl phthalate with ethylene diamine and benzil in ethanol at 25 °C.

Synthesis of Schiff bases:

The Schiff bases were synthesised by the condensation of acid hydrazide and benzil (1:1),(2:1),(2:2), dissolved in ethanol. After the condensation of the solution, the precipitate was separated, filtered, washed with ethanol and dried over CaCl₂ in vacuum.

Synthesis of the complexes :

Different procedures were used for the preparation of the complexes. An ethanolic (25 ml) solution of schiff base (0.001 mol, 0.002 mol) was mixed with zinc (II) chloride (0.001 mol) or (0.002 mol) ethanolic solution keeping ligand-metal ratio 1:1,1:2 and 2:1. The mixture of reaction was then refluxed for 3hr. The complexes were precipitated upon concentration of the solution and cooling in ice. The compounds separated were filtered, washed with cold ethanol and dried over CaCl_2 in a vacuum. The preparation of the complexes of the types $[\text{ZnL}(\text{Succ})]$ and $[\text{Zn}_2(\text{L})_2(\text{Succ})\text{Cl}_2]$ were carried out by refluxing (0.001 mol) and (0.002 mol) of $[\text{ZnLCl}_2]$ with (0.001 mol) succinic acid disodium salt in ethanol-DMF for about 2hrs. (0.001 mol) acetyl acetone was added to mixture of (0.001 mol) $[\text{Zn}_2\text{LCl}_4]$ dissolved in ethanol-DMF and refluxed for about 1.30 – 2 hrs and on cooling precipitation of the complexes of both methods takes place. The separated complexes were filtered off, washed with cold ethanol and dried.

Physical measurements :

Elemental analysis were performed gravimetrically. The IR spectra of the samples were recorded using the KBr disc (4000-400) cm^{-1} FT-IR spectrophotometer. Molar conductivity were measured in freshly prepared 10^{-3} mol solution in DMF at room temperature with conductivity meter consort LF-42. Chlorine was determined gravimetrically as AgCl. The UV spectra in the range (1100-200)nm range were obtained in DMF on a shmadzu UV-1650 pc spectrophotometer.

Results and Discussion

The template condensation of Schiff base ligand in the presence of zinc(II) chloride produced new metal complexes. The newly synthesized mono and binuclear Schiff base complexes are very stable at room temperature in the solid state. These chelates are generally soluble in DMF. The elemental analytical data of the complexes revealed that the compounds have a metal-ligand stoichiometry of 1:1,2:1 and 1:2. The analytical data are in good agreement with proposed stoichiometry of the complexes. The colours, melting points, IR and UV spectral data of all the compounds are presented in (Table 1-4). The conductivity values for the $[\text{ZnL}_3]\text{Cl}_2$, $[\text{ZnL}_4]\text{Cl}_2$ complexes ($150,155 \text{ ohm}^{-1}.\text{cm}^2.\text{mol}^{-1}$) indicate their electrolytic behaviour. This suggests that the anion (Cl) is ionically bonded in the outer sphere of coordination. On the other hand conductivity values measured under the same conditions for the other complexes ($8-40 \text{ ohm}^{-1}.\text{cm}^2.\text{mol}^{-1}$) indicate that the complexes are non electrolytic in DMF solution. This suggests that the chloride ion are covalently bonded⁽¹⁹⁾. The formation of the metal-ligand bonds and the

sites of coordination in the ligands were studied by spectral means. The IR spectra of the complexes are compared with that of the free ligand to determine the changes that might have taken place during the complexation Table(3). In the infrared spectra of the complexes, the NH₂ and C=O stretching frequencies of ethylene diamine and benzil or acetylacetone are absent with the appearance of new sharp band at 1595–1620 cm⁻¹, characteristic of the azo methane nitrogen present in the free ligand. The lowering in this frequency region by 15-20 cm⁻¹ indicates the condensation of carbonyl and amino groups with the involvement of the nitrogen atom of the azo methine $\nu(\text{C}=\text{N})$ group in complex formation^(20,21). The infrared absorption spectral of the ligands show the characteristic bands at 1635-1670 and 3310-3300 cm⁻¹ due to (C=O) stretching and NH₂ bending vibration, respectively⁽²²⁾. In the spectra of complexes negative shift of about 15-32 cm⁻¹ and 110-130 cm⁻¹ were observed in the (C=O) stretching for cyclic (and noncyclic) complexes and NH₂ bending for noncyclic complexes vibrations respectively. These negative Shifts of (C=O) and NH₂ bands can be regarded as evidence for coordination through carbonyl oxygen and terminal ethylene diamine nitrogen atoms⁽²³⁾. Further support for this coordination were indicated by the appearance of new bands 440-448 and 410-415 cm⁻¹ in the infrared of the complexes are assigned to M-O and M-N stretching vibration, respectively⁽²⁴⁾. The bands due to (C=O) and NH amide stretching vibrations located at 1635-1670 and 3285-3297 cm⁻¹ in the free ligands spectra were remain unaffected upon macrocyclic [ZnLCl₂] and [ZnL]Cl₂ complexes formation (where L=L₇, L₈, L₉) indicating the non-involvement of carbonyl oxygen atom coordination, beside the NH-amide vibration band remain unchanged on all complexes.

Table (1) : Some physical properties and name of the ligands

No.	Benzil mol	Acid hydrazide mol	m.p C ^o	Color	Name
L ₁	0.01	0.01	190	Pale Purple	Benzilidene malonyl bis (ethylene diamine).
L ₂	0.01	0.01	185	Lemon Yellow	Benzilidene succinyl bis(ethylene diamine).
L ₃	0.01	0.01	195	Pale yellow	Benzilidene phthaloyl bis(ethylene diamine).
L ₄	0.01	0.02	215	Pale Purple	Benzilidene dimalonyl tetra (ethylene diamine).
L ₅	0.01	0.02	220	Pale yellow	Benzilidene disuccinyl tetra (ethylene diamine).
L ₆	0.01	0.02	235	Pale yellow	Benzilidene diphthaloyl tetra (ethylene diamine).
L ₇	0.02	0.02	240	Pale Purple	Di(benzilidene malonyl) tetra(ethylene diamine).
L ₈	0.02	0.02	248	Pale yellow	Di(benzilidene succinyl) tetra (ethylene diamine).
L ₉	0.02	0.02	239	Pale yellow	Di(benzilidene diphthaloyl) tetra (ethylene diamine).

Table (2) : Analytical and some physical data of the complexes

No.	Complex	m.p C°	%M (Calc.)	Λ_m in DMF $\text{ohm}^{-1}.\text{cm}^2.$ mol^{-1}	% Cl (Calc.)
1	[Zn(L ₁)Cl ₂]	205	(13.12)12.91	30	(14.25)14.13
2	[Zn(L ₂)Cl ₂]	203	(12.76)12.33	25	(13.86)13.61
3	[Zn(L ₃)Cl ₂]	207	(11.67)11.52	150	(12.67)12.65
4	[Zn ₂ (L ₄)Cl ₄]	225	(15.89)15.77	38	(17.26)17.14
5	[Zn ₂ (L ₅)Cl ₄]	238	(15.36)15.32	18	(16.69)16.35
6	[Zn ₂ (L ₆)Cl ₄]	252	(13.81)13.61	16	(14.99)14.78
7	[Zn(L ₇)Cl ₂]	255	(7.60) 7.50	23	(8.25)7.94
8	[Zn(L ₈)Cl ₂]	258	(7.36) 7.96	36	(7.99)7.87
9	[Zn(L ₉)Cl ₂]	252	(6.64) 6.52	155	(7.12)7.10
10	[Zn(L ₁)(suc)]	227	(12.03)11.98	10	-
11	[Zn(L ₂)(suc)]	260	(11.73)11.71	8	-
12	[Zn ₂ (L ₁) ₂ (suc)Cl ₂]	250	(12.55)12.43	28	(6.82)6.61
13	[Zn ₂ (L ₂) ₂ (suc)Cl ₂]	246	(12.22)12.11	32	(6.64)6.33
14	[Zn ₂ (L ₁₀)Cl ₄]	261	(14.75)13.93	15	(16.01)15.83
15	[Zn ₂ (L ₁₁)Cl ₄]	257	(14.29)14.17	40	(15.52)15.41

The symmetric ($-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}$) stretching band carboxylate group shifted to lower frequency region in the spectra of complexes while the asymmetric ($-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}$) stretching band shifted to higher frequencies, the value of $\Delta\nu$ about 150 cm^{-1} , suggesting coordination of one carboxylate oxygen atom⁽²⁵⁾. The other new band located at 570 cm^{-1} assigned for chloride. The shape and position of this band suggested the non-involvement of this group in coordination⁽²⁶⁾ and therefore remain outside the coordination sphere. These observations are in agreement with the conductance data and support the given formulation of the complexes. The electronic spectra of the zinc(II) chloride complexes, in addition to the bands observed at $28571-40000 \text{ cm}^{-1}$, due to $\pi \rightarrow \pi^*$ transitions in the free ligands, the UV spectra of the zinc(II) complexes showed additional bands in the range $28291-40122 \text{ cm}^{-1}$ assigned to charge transfer transition from filled orbitals of the ligand to the vacant π orbitals of the metal and thus supporting the formation of complexes. Sometimes the ligands are characterized by two absorption bands in the UV-region. A high intensity band and a second band with lower intensity, both bands showed red shift on coordination with metal ion. These observation represent other indication for the coordination of the ligand to the metal ion^(27,28). The UV spectra of the complexes are summarized in Table (4).

Conclusion

Zn(II) is effective as a template for the Schiff base condensation of benzil-acid hydrazide with ethylene diamine ligands yielding new complexes. Zn(II) complexes have been synthesized using the Schiff base

ligands and characterized on the basis of analytical and spectral data. The Schiff bases coordinate through azo methine nitrogens to the metal ion and act as tetra and doctadentate ligands. The complexes exhibit tetra and octahedral configuration as shown in fig (I),(II),(III)

Table(3) : The most important IR bands(cm^{-1}) of the ligands and their complexes

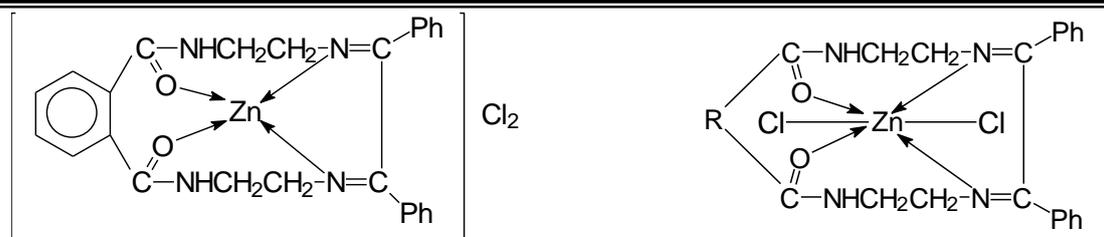
Compound	N-H amide	ν C=O	ν C=N	M-O	M-N	ν Cl	ν NH ₂	ν asCOO ⁻	ν s COO ⁻	ν NH
L ₁	3295	1660	1620							
[Zn(L ₁)Cl ₂]	3293	1640	1605	440	410					
L ₂	3294	1665	1595							
[Zn(L ₂)Cl ₂]	3292	1633	1580	440	412					
L ₃	3285	1670	1630							
[Zn(L ₃)]Cl ₂	3280	1655	1610	448	410	575				
L ₄	3288	1650	1595				3300			
[Zn ₂ (L ₄)Cl ₄]	3286	1630	1575	440	410		3180			
L ₅	3297	1660	1595				3310			
[Zn ₂ (L ₅)Cl ₄]	3295	1630	1580	445	415		3200			
L ₆	3290	1670	1610				3310			
[Zn ₂ (L ₆)Cl ₄]	3290	1650	1590	440	410		3180			
L ₇	3290	1635	1595							
[Zn(L ₇)Cl ₂]	3288	1635	1575		410					
L ₈	3296	1641	1595							
[Zn(L ₈)Cl ₂]	3292	1640	1575		410					
L ₉	3290	1660	1610							
[Zn(L ₉)]Cl ₂	3288	1658	1590		410	575				
[Zn(L ₁)(suc)]	3290	1640	1605	440	410			1555	1405	
[Zn(L ₂)(suc)]	3292	1633	1580	440	410			1556	1406	
[Zn ₂ (L ₁)(suc)Cl ₂]	3290	1640	1605	440	410			1560	1410	
[Zn ₂ (L ₂)(suc)Cl ₂]	3292	1633	1580	440	410			1558	1409	
[Zn ₂ (L ₁₀)* Cl ₄]	3285	1630	1575	442	412					3185
[Zn ₂ (L ₁₁)** Cl ₄]	3290	1650	1590	440	410					3190

*L₁₀ = Benziliden dimalonyl tetra (ethylenediamine) acetyl acetone.

**L₁₁ = Benziliden disuccinyl tetra (ethylenediamine) acetyl acetone.

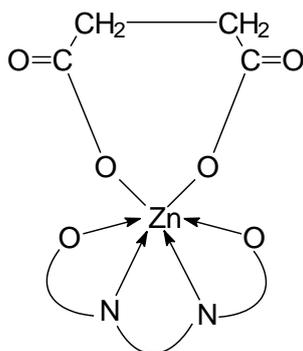
Table(4): Electronic spectral data of the complexes

No.	Electronic spectra (cm^{-1})
1	31846,367503
2	32752,40007
3	31322,32653
4	29361,36532
5	31665,40012
6	28291,38313
7	30774,36853
8	32788,40122
9	32171,39862
10	27691,33662
11	28744,37013
12	27342,35623
13	30451,33812
14	27182,37355
15	27659,35625



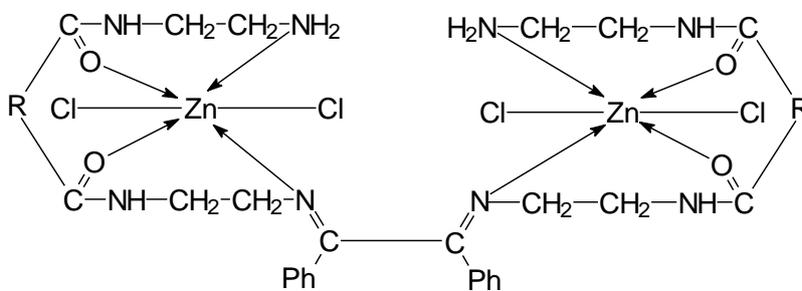
$[Zn(L_b)Cl_2]$
 $L_b=L_3$

$[Zn(L_a)Cl_2]$
 $L_a=L_1, L_2$
 $R=CH_2, C_2H_4$

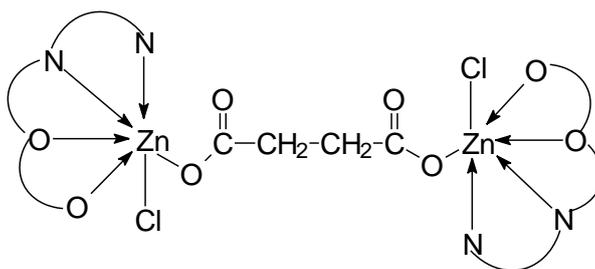


$[Zn(L_a)(suc)]$
 Suc=Succinate ion

Fig (1)

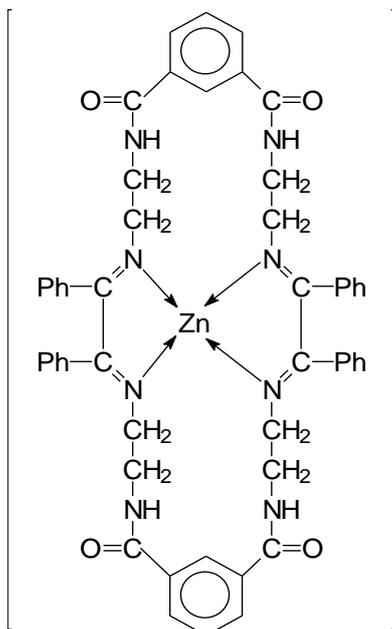


$[Zn_2(L_c)Cl_4]$
 $L_c=L_4-L_6$
 $R=C_6H_4, C_2H_4, CH_2$

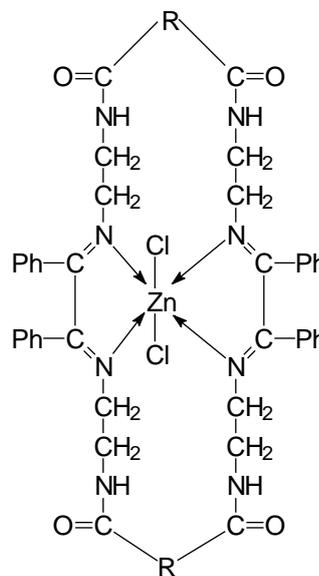


$[Zn_2(L_a)_2(Succ)Cl_2]$

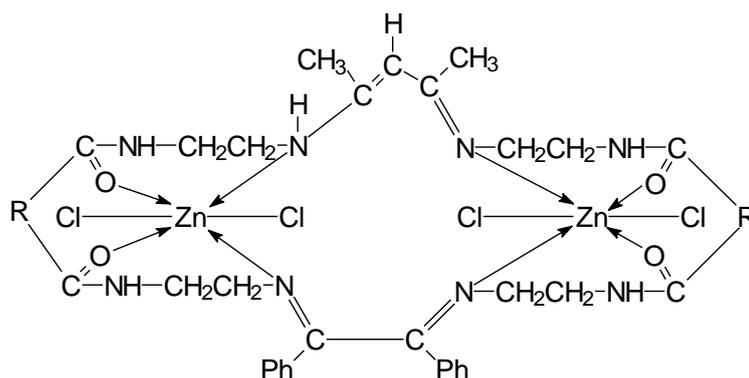
Fig (II)



$[Zn(L_E)]Cl_2$
 $L_E = L_9$



$[Zn_2(L_d)Cl_4]$
 $L_d = L_7, L_8$
 $R = CH_2, C_2H_4$



$[Zn_2(L_g)Cl_4]$
 $L_g = L_{10}, L_{11}$
 $R = CH_2, C_2H_4$
 Fig(III)

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