

COMPLEXES OF Mn (II), Zn (II), Hg (II) AND Fe (III) WITH N, N'-BIS (R-PHENYL) ETHANEDIIMINE

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The synthesis and characterisation of complexes of N, N-Bis (R-phenyl) ethanediimine Schiff bases (R=*o*-OH L₁,=*p*-OH L₂,=*p*-OCH₃ L₃) with Mn (II), Zn (II), Hg (II) and Fe (III) have been described. Characterisation of the complexes has been accomplished primarily by elemental analysis, molar conductance as well as electronic and infrared spectral measurements. Formation, stoichiometry and stability of the complexes have been tested in solution using electronic spectral measurements. It is concluded that the ligands (L₁-L₃) are coordinated to the metal ions as bidentate NN ligands. The complexes are suggested to exhibit a distorted octahedral geometry.

Key words. Complexes, Schiffbases, Transition metals, Ethanediimine derivatives.

Introduction

The chelating properties of Schiff bases towards transition metal ions were of interest of many authors [1-12]. The ability of Schiff bases to form metal complexes was based on their tendency to coordinate with metal ions through the N-atom lone pair. The condensation product of glyoxal and *o*-aminophenol, N, N-bis (*o*-hydroxyphenyl) ethanediimine has long been used as ion exchanger in the recovery of heavy metals [13]. However, no structural studies on the complex of this and similar ligands seems to have been carried out so far. In this paper, the complexes of entitled ligands with Mn (II), Zn (II), Hg (II) and Fe (III) have been prepared and characterised using several tools e.g. elemental analyses, molar conductance, electronic and infrared spectral measurements.

Experimental

Glyoxal and (*o*-OH, *p*-OH and *p*-OCH₃) aniline were of reagent grade. The ligands (L₁-L₃) were prepared by condensation of glyoxal with the corresponding amine in 1:2 proportions in ethanol. The purity of the synthesized compounds was checked by thin layer chromatography [6,14] using plates of silica gel. The structures were confirmed by microanalysis and infrared spectra (Tables 1,3). The agreement between the

obtained (Table 4) and reported [6,14] absorptivity values suggested that L₁-L₃ are pure compounds.

The solid complexes were prepared by mixing a hot ethanolic solution of metal salt (MnCl₂·4H₂O, ZnCl₂, HgCl₂ and FeCl₃·6H₂O) with a hot stirred ethanolic solution of the ligand in the ratios 1:1 and/or 1:2 metal:ligand. The mixture was refluxed over a water bath for 4 hrs and then allowed to evaporated to a small volume. The solid complex produced was filtered off, washed with ethanol and finally with acetone and stored in a desiccator over dry silica gel.

Physical measurements. The molar conductances of the complexes (1×10⁻³M) were measured using WPA, Saffron Walden CM 25 conductivity meter with a cell constant 1.48 cm⁻¹. Infrared spectra of the complexes were recorded on Perkin-Elmer 599 infrared spectrophotometer as KBr discs. The electronic spectra were recorded on Cecil CE 599 recording spectrophotometer using 1.0 cm matched silica cells.

Results and Discussion

The complexes isolated are given in Table 2. The elemental analysis data given in that Table reveal that the neutral molecules of the ligands (L₁-L₃) are coordinated to the metal ions. The general formula of 1:1 complexes is [M(L)X₂(H₂O)₂] where M=Mn (II), Zn (II) and Hg (II) and for 1:2 complexes, the general formula in [M(L)₂X₂]X where M=Fe (III) and X=Cl⁻.

Molar conductance values of 1×10⁻³M solutions of the complexes in methanol (Table 2) lies in the range 48-139 for 1:1 complexes and between 148-207 ohm⁻¹ cm²mole⁻¹ for 1:2 types. The reported [15] values are 100 and 200 ohm⁻¹ cm²mole⁻¹ for 1:1 and 1:2 electrolytes respectively. Accordingly, it can be deduced that the conductivity results in consistent within the suggested formula given before but some ionic dissociation takes place in methanol.

TABLE 1. MICROCHEMICAL ANALYSES DATA FOR THE LIGANDS L₁-L₃.

Compound	Calculated (found)%		
	C	H	N
C ₁₄ H ₁₂ N ₂ O ₂	69.99	5.03	11.66
(R= <i>o</i> -OH)	(69.50)	(6.50)	(11.00)
C ₁₄ H ₁₂ N ₂ O ₂	69.99	5.03	11.66
(R= <i>p</i> -OH)	(71.70)	(5.90)	(10.30)
C ₁₆ H ₁₆ N ₂ O ₂	71.62	6.01	10.44
(R= <i>p</i> -OCH ₃)	(69.20)	(5.80)	(10.00)

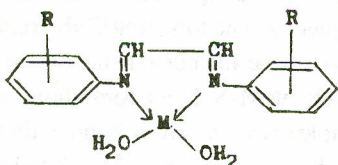
Infrared spectra. Assignment of the important infrared bands are presented in Table 3. The spectra of free ligand, L_1 , (R=*o*-OH) shows a sharp band at 3412 cm^{-1} due to O-H stretching frequency. Its complexes L_1 -Mn (II) and L_1 -Zn (II) show a strong sharp band at 3370 and 3340 cm^{-1} respectively indicating that O-H group is not involved in bonding with the metal. A typical observation was reported [6] for the solid complexes of L_1 with Cu (II), Co (II), Ni (II) and UO_2 (II) and also for L_1 -Th(IV) complex [16]. On the other hand, the spectrophotometer determined high pK_a value (12.16 ± 0.05) [14] for the two *o*-OH groups of L_1 indicated a difficult contribution of such groups in coordination to the metal ion. With respect to the complexes L_1 -Hg (II), L_1 -Fe (III), the free O-H band is presumably to be buried under the strong broad band due to absorption of water molecules. The broad trough band appeared around 3430 , 3400 , 3340 and 3300 cm^{-1} for the

complexes of L_1 with Mn (II), Zn (II), Hg (II) and Fe (III) respectively are assigned to the coordinated water. The existence of water molecules is further substantiated from the results of elemental analysis (Table 2). With respect to ligand L_2 (R=*p*-OH), the stretching vibration bands of free *p*-OH groups appeared as a broad band at 3150 cm^{-1} . The strong band observed in the region 1600 - 1620 cm^{-1} in the spectrum of the free ligands (L_1 - L_2) is assigned to the azomethine (C=N)[17] stretching frequency. The lowering C=N frequency on chelation may tentatively be attributed to the lowering of C=N bond order as a result of M-N bond formation. The far infrared spectra of complexes show strong band in the region 500 - 755 cm^{-1} which can be assigned [18] to M-N bond with azomethine group and M-O bond with the coordinated water molecule. The observed band at 1445 - 1580 cm^{-1} in the spectra of free ligands and at 1400 - 1565 cm^{-1} complexation can be assigned

TABLE 2. ANALYTICAL DATA, COLOUR, MELTING POINT AND MOLAR CONDUCTANCE VALUES ($\text{Ohm}^{-1}\text{mol}^{-1}\text{.cm}^2$) OF THE DIFFERENT COMPLEXES.

Complexes	Colour	M.P. °C	Mol. conduc.	%Calc. (found)			
				C	H	N	Cl
Complexes of $H_2L_1(o\text{-OH})$							
$[\text{Mn}(\text{H}_2\text{L}_1)\text{Cl}_2(\text{H}_2\text{O})_2]4\text{H}_2\text{O}$	Brown	>300	139.10	35.46 (35.92)	5.10 (4.87)	5.91 (5.46)	14.95 (14.39)
$[\text{Zn}(\text{H}_2\text{L}_1)\text{Cl}_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$	Black	>300	63.64	37.48 (38.01)	4.49 (5.01)	6.25 (6.00)	15.81 (16.46)
$[\text{Hg}(\text{H}_2\text{L}_1)\text{Cl}_2(\text{H}_2\text{O})_2]4\text{H}_2\text{O}$	Black	>300	62.16	27.13 (26.93)	3.70 (4.10)	4.52 (4.00)	11.44 (10.73)
$[\text{Fe}(\text{H}_2\text{L}_1)\text{Cl}_3(\text{H}_2\text{O})]4\text{H}_2\text{O}$	Black	>300	51.36	34.14 (34.64)	4.50 (4.70)	5.69 (5.22)	21.59 (21.32)
$[\text{Fe}(\text{H}_2\text{L}_1)_2\text{Cl}_2(\text{H}_2\text{O})_2]\text{Cl}.4\text{H}_2\text{O}$	Black	>300	207.2	47.05 (46.77)	4.51 (4.60)	7.84 (7.00)	14.88 (15.24)
Complexes of $H_2L_2(p\text{-OH})$							
$[\text{Mn}(\text{H}_2\text{L}_2)\text{Cl}_2(\text{H}_2\text{O})_2]4\text{H}_2\text{O}$	Black	>300	127.3	35.46 (35.00)	5.10 (4.90)	5.91 (5.40)	14.95 (14.62)
$[\text{Zn}(\text{H}_2\text{L}_2)\text{Cl}_2(\text{H}_2\text{O})_2]4\text{H}_2\text{O}$	Black	>300	57.72	34.70 (35.20)	4.99 (5.10)	5.78 (6.00)	14.63 (14.46)
$[\text{Hg}(\text{H}_2\text{L}_2)\text{Cl}_2(\text{H}_2\text{O})_2]4\text{H}_2\text{O}$	Black	>200	71.04	27.13 (27.92)	3.90 (4.23)	4.52 (4.90)	11.44 (11.13)
$[\text{Fe}(\text{H}_2\text{L}_2)\text{Cl}_3(\text{H}_2\text{O})]4\text{H}_2\text{O}$	Black	>300	48.84	34.14 (35.10)	4.50 (4.60)	5.69 (5.63)	21.59 (21.44)
$[\text{Fe}(\text{H}_2\text{L}_2)_2\text{Cl}_2]\text{Cl}.4\text{H}_2\text{O}$	Black	>300	148.0	47.05 (48.10)	4.51 (4.80)	7.84 (7.50)	14.88 (14.96)
Complexes of $L_3(p\text{-OCH}_3)$							
$[\text{Mn}(\text{L}_3)\text{Cl}_2(\text{H}_2\text{O})_2]$	Black	200	137.6	44.67 (45.01)	4.69 (5.10)	6.51 (6.40)	16.48 (16.36)
$[\text{Zn}(\text{L}_3)\text{Cl}_2(\text{H}_2\text{O})_2]4\text{H}_2\text{O}$	Black	>300	99.16	37.48 (36.90)	5.15 (4.94)	5.46 (5.53)	13.83 (14.70)
$[\text{Hg}(\text{L}_3)\text{Cl}_2(\text{H}_2\text{O})_2]4\text{H}_2\text{O}$	Black	180	71.04	29.66 (30.54)	4.36 (4.60)	4.32 (4.87)	10.94 (9.35)
$[\text{Fe}(\text{L}_3)_2\text{Cl}_2]\text{Cl}.4\text{H}_2\text{O}$	Black	210	207.0	49.86 (48.80)	5.23 (5.00)	7.27 (7.50)	13.80 (14.14)

to C=C in plane vibration of aromatic system conjugated to azomethine group. The similarity of the infrared spectra of the complexes suggests that the mode of coordination of the ligands is the same in all complexes irrespective of the metal ions used. It is concluded that the ligands (L_1 - L_3) are coordinated as neutral bidentate ligands using the two central azomethine nitrogens where a five membered chelate ring is formed as represented below:



R=*o*-OH, *p*-OH and *p*-OCH₃.

Electronic spectra. The electronic spectral data of the ethanolic solutions of free ligands (L_1 - L_3) and their 1:1 complexes are given in Table 4. The strong band observed at 298 nm for L_1 (R=*o*-OH) is assigned to $\pi - \pi^*$ of the central C=N groups. The lowest excitation energy band comprised by the free ligands L_2 (R=*p*-OH) and L_3 (R=*p*-OCH₃) at 390 and 380 nm respectively is assigned to an intramolecular charge transfer transition taking place within the ligand molecule [19]. On complexation, the spectra of L_1 - L_3 are practically unchanged reveal noninstantaneous complex formation. The only exception is that in the case of 1:1 L_1 -Fe (III) solution, a very strong shoulder is appeared at ~350 nm. The absence of an intramolecular charge transfer band in the electronic spectra of L_1 is ascribed mainly to the difficult intramolecular charge trans-

TABLE 3. INFRARED SPECTRAL DATA OF THE FREE LIGANDS AND THEIR METAL COMPLEXES.

Free ligands	Metal complex					
	Mn(II)	Zn(II)	Hg(II)	Fe(III)		
L_1 (<i>o</i> -OH)	3412 s	3370 s	3340 s	3340 b	3300 vb	ν_{O-H} and H_2O
		3430 b	3400 b	—	—	
L_2 (<i>p</i> -OH)	3150 b	3350 vb	3250 vb	3200 b	3250 vb	$\nu_{C=N}$
L_3 (<i>p</i> -OCH ₃)	—	3400 b	3400 vb	3400 b	3350 vb	
L_1	1620	1605	1610	1605	1595	
L_2	1612	1600	1595	1605	1590	$\nu_{C=C}$ aro- matic
L_3	1600	1615	1605	1605	1605	
L_1	1510	1495	1500	1495	1525	
	1445	1435	1435	—	1400	ν_{M-N}
L_2	1580	1510	1510	1510	1565	
	1510	1495	1430	1455	1510	
L_3	1575	1515	1505	1510	1500	ν_{M-N}
	1470	1505	—	1460	—	
L_1	—	725	720	745	755	
L_2	—	510	—	500	750	ν_{M-N}
L_3	—	730	735	730	725	

s=sharp, b=broad, vb=very broad.

fer transition in the molecule of L_1 due to its entirely nonplanar structure [20]. However, the observed intramolecular CT transition band at ~350 nm in the spectra of L_1 -Fe (III) complex solution can be likely explained on the principle of the expected forced some planarity of L_1 due to its coordination to Fe (III) ion, i.e. easier intramolecular CT transition.

Job's [21] continuous variation method was applied to establish the composition of L_1 -Fe (III) complex in solution [21]. The method (Table 5) revealed 1:1 stoichiometry as shown in Fig. 1 (a,b). The stability of this complex was inspected by determining its apparent formation constant

TABLE 4. λ_{max}^{nm} AND $10^{-3}\epsilon_{max}$, mole⁻¹ cm² (IN BRACKETS) VALUES OF THE ABSORPTION BANDS OF THE LIGANDS AND OF THEIR 1:1 METAL COMPLEX ETHANOLIC SOLUTIONS.

Free ligands	Mn(II)	Zn(II)	Hg(II)	Fe(III)
L_1 (<i>o</i> -OH) ^x				
217(19.50)	—	—	—	—
240(11.63)	236(9.28)	236(9.48)	—	—
298(7.56)	292(6.00)	293(6.15)	294(6.70)	294(9.18)
—	—	—	—	350sh(1.93)
L_2 (<i>p</i> -OH) ^y				
247(10.10)	—	—	—	240(15.60)
300(5.70)	304(5.55)	304(5.40)	300(5.85)	293(9.80)
390(23.00)	386(10.00)	386(9.73)	386(9.95)	385(23.40)
L_3 (<i>p</i> -OCH ₃) ^y				
240(12.00)	—	—	—	233(16.90)
300(7.45)	303(4.98)	303(5.20)	300(5.53)	290(10.30)
380(22.80)	376(6.55)	376(6.75)	376(6.75)	372(20.50)

Sh=Shoulder; x=1x10⁻⁴M and y=5x10⁻⁵M

TABLE 5. DATA OF THE CONTINUOUS VARIATION METHOD FOR THE L_1 -Fe(III) COMPLEX AT 25°C.

Spectra No.	[Fe(III)]x10 ⁴ M	[L_1]x10 ⁴ M	Mole fraction of Fe (III)	Absorbance at 324 nm
1	0.20	1.80	0.10	0.07
2	0.40	1.60	0.20	0.14
3	0.50	1.50	0.25	0.16
4	0.60	1.40	0.30	0.20
5	0.80	1.20	0.40	0.27
6	0.90	1.10	0.45	0.29
7	1.00	1.00	0.50	0.43
8	1.10	0.90	0.55	0.37
9	1.20	0.80	0.60	0.42
10	1.40	0.60	0.70	0.51
11	1.50	0.50	0.75	0.57
12	1.60	0.40	0.80	0.62
13	1.70	0.30	0.85	0.66
14	1.80	0.20	0.90	0.72
15	1.90	0.10	0.95	0.83

[9,11] value utilizing the result of the continuous variation method. The value obtained is 1×10^4 which imply that the complex has a moderate stability.

Geometry of the complexes. The visible spectra of $(1-2) \times 10^{-4} \text{M}$ ethanolic solutions of the different synthesized complexes were recorded covering the range 200-700 nm (Fig.2). The λ_{max} and ϵ_{max} values of the observed different absorption bands are listed in Table 6. The one or two broad bands or shoulders appeared in the range 340-482 nm can be assigned to an intramolecular charge transfer transition within

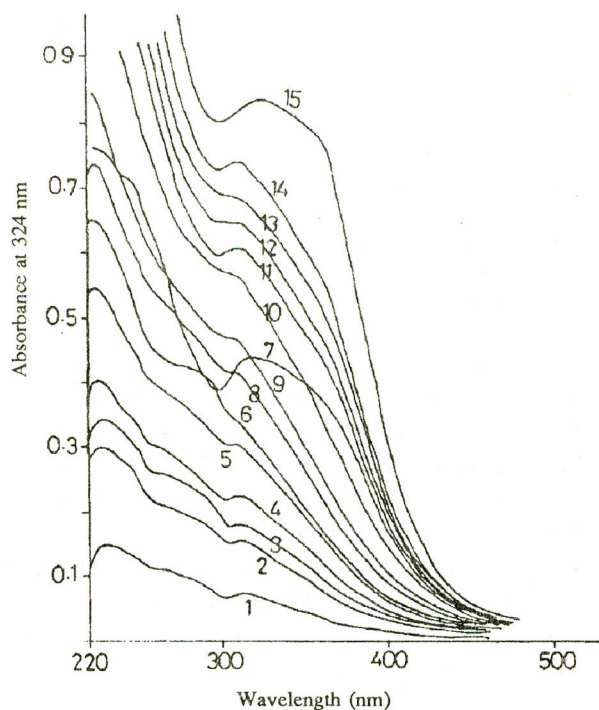


Fig. 1a. Electronic spectra of L_1 (R=O-OH) + Fe(III) complex solutions (continuous variation method).

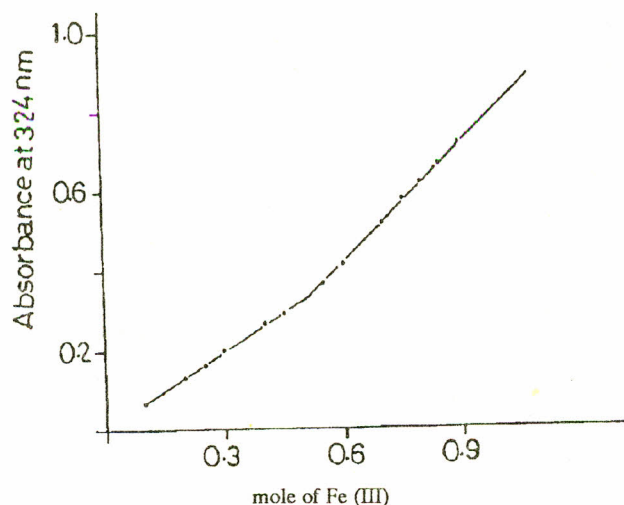


Fig. 1b. Job's continuous variation plot of L_1 -Fe(III) complex.

the complexed ligand molecule, i.e. L-MCT transtion. This assignment is based on the evidence that such bands are characterised by high molar extinction; coefficients $(1.38-15.10) \times 10^3 \text{ mole}^{-1} \text{ cm}^2$ as well as the fact that this type of electronic transition is expected to be easier in the complexed ligands due to the positive charge of the coordinated metal ion. The longer wavelength side of the L-MCT band is associated with a long tail into the low energy region 500-600 nm which may suggests an octahedral structure for these complexes [22]. The relatively high molar absorption of these

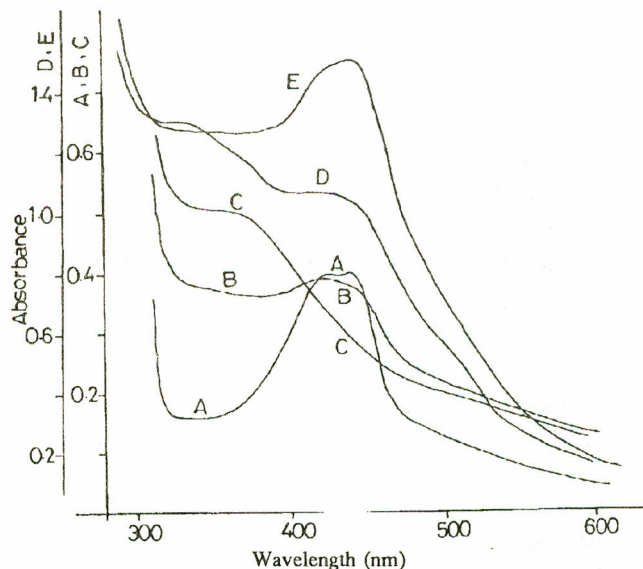


Fig. 2. uv-Visible absorption spectra of $1 \times 10^{-4} \text{M}$ ethanolic solutions of L_1 (R=O-OH) complexes with A: Mn(II), B: Zn(II), C: Hg(II), D: Fe(III), $2 \times 10^{-4} \text{M}$ and E: $(L_1)_2$ -Fe(III).

TABLE 6. ELECTRONIC SPECTRAL DATA OF METHANOLIC SOLUTIONS OF THE DIFFERENT COMPLEXES.

Complex	λ_{max} , nm	$10^{-3} \epsilon_{\text{max}}$
L_1 -Mn(II) ^x	430 b	2.00
L_1 -Zn(II) ^x	427 b	1.95
L_1 -Hg(II) ^x	370 b	2.53
L_1 -Fe(III) ^y	340 sh	6.35
$(L_1)_2$ -Fe(III) ^x	430 b	5.20
$(L_1)_2$ -Fe(III) ^x	434 b	15.10
L_2 -Mn(II) ^z	482 vb	4.70
L_2 -Zn(II) ^z	430 vb	2.48
L_2 -Hg(II) ^z	420 sh	1.64
L_2 -Fe(III) ^y	340 sh	7.28
$(L_2)_2$ -Fe(III) ^z	360 sh	9.90
L_3 -Mn(II) ^z	420 sh	1.38
L_3 -Zn(II) ^z	420 b	1.73
L_3 -Hg(II) ^z	418 b	2.80
$(L_3)_2$ -Fe(III) ^z	360 sh	7.30

b=broad, vb=very broad, sh=shoulder and ϵ_{max} =in $\text{mol}^{-1} \text{cm}^2$; x= $1 \times 10^{-4} \text{M}$, y= 2×10^{-4} , and z= $5 \times 10^{-5} \text{M}$.

bands can be attributed to the expected a centric structure of these complexes, i.e. distorted octahedral structure [23].

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