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PHYSICOCHEMICAL STUDIES OF IRON (III) COMPLEXES AND SCHIFF BASE LIGANDS DERIVED FROM AN ALDEHYDE

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ABSTRACT

Iron (III) Complexes of the type M(Ligand^1-Ligand^4),have been synthesized from Schiff bases derived from 2-hydroxy-1-naphthaldehyde.The complexes were characterized using microanalysis, infrared, UV/visible and molar conductivity. Microanalysis results have revealed that the metal (III) complexes were formed in 1:2 molar ratio (Metal: Ligands). Infrared studies have showed that the complexes coordinated through the azomethine nitrogen and phenolic oxygen of the ligands. The UV/ visible showed broad bands in the visible region which were probably due to d-d transitions of the metal ions. Molar conductivity results showed that the complexes were non-electrolytes.

Keywords: Complex compounds, infra red, micro analysis, naphthaldehyde, synthesis, uv/visible.

INTRODUCTION

Schiff bases are organic compounds having an azomethine group (>C=N). Various Studies have shown that >C = N group have considerable biological importance. Schiff bases can be considered as useful chelating agents when a suitable functional group such as – OH, - SH, - NH_2, etc, are present sufficiently close to the azomethine group. Metal complexes with Schiff bases have occupied an important place in the development of coordination chemistry due to its interesting structural features and important applications [1]. Thus, this study is to synthesize some Schiff base ligands and their transition metal (III) complexes and to characterize the ligands and their complexes using solubility, conductivity, melting point, infrared spectroscopy UV and microanalysis of the compounds.

EXPERIMENTAL

All chemicals and solvents used were of analar grade while 2-hydroxy-1-naphthaldehyde and the amines were obtained from sigma–aldrich and were used without purification. the metal (iii) salts was used as chloride. ir spectra were recorded on a shimadzu London ftir-8400s spectrophotometer at narict, zaria in the range 4000-500 cm^{-1} as kbr pellets. uv/ visible spectra were obtained at narict, zaria, on a u/v 2500pc series double-beam spectrophotometer. c, h and n analyses was done by medac ltd in uk. molar conductance of the ligands and complexes were determined in soil science department, university of maiduguri, on a metler p163 (r) series model ec 500. Melting pints were recorded on a griffin melting point apparatus at Faculty of Pharmacy, University of Maiduguri, Nigeria, and are uncorrected.

Preparation of the ligands

All the ligands (L^1-L^4) were prepared as described by Zahid et al. [2]. 2-hydroxy 1-naphthaldehyde (10 mmol, 1.728 g) was dissolved in 20 ml of ethanol. The ethanolic solution was added to each of the selected amines: 2 aminophenol (10 mmol,1.09 g), 2-nitroaniline (10 mmol,1.38 g), p-methyl aniline (10 mmol, 1.07 g), and aniline (10 mmol, 0.93 g) in 20 mL of ethanol respectively, followed by addition of 3-4 drops of conc. H_2SO_4. The mixture was refluxed for about 3-4 hours using hot plate magnetic stirrer. The product obtained was washed with diethyl ether, followed by drying in a desiccator over fused $CaCl_2$.This processes gave the Schiff base ligands: L^1-L^4. The pure and dried Schiff bases (L^1-L^4) were characterized using IR, Uv/visible, meltings points, molar conductance, solubility and microanalysis.

Preparation of the complexes

The complexes were prepared using a literature procedure [3], by reacting 1:2 mole ratios (metal: ligand). $FeCl_3.6H_2O$ (5 mmol, 1.35 g). This was weighed and dissolved in 20 ml of distilled water and added gradually to 20 ml ethanolic solution of the ligands. Each mixture was refluxed for about 3-4 hours using a hot plate magnetic stirrer. The product obtained was cooled using ice and left to stand for 24 hours and the coloured crystals separated, this was filtered and the product obtained was washed with diethyl ether and dried over fused $CaCl_2$ in a desiccator. The pure complexes were characterized using IR, Uv/visible, melting points, molar conductance, solubility and microanalysis.

RESULTS AND DISCUSSION

Table 1: Relevant infrared (IR) frequencies (cm^{-1}) for the Schiff base ligands and their metal (III) complexes.

Compound	V(OH)	V(C-O)	V(C-N)	V(C=N)	V(N-O)	V(M-N)	V(M-O)
L^1	3410s	1251m	1410b	1626sh	1140s	-	-
L^2	3472s	1248m	1331w	1612s	1155w	-	-
L^3	3453s	1240m	1314m	1624sh	1168m	-	-
L^4	3424b	1329s	1422w	1617s	1143b	-	-
$Fe(L^1-L^1)$	3446b	1247w	1358b	1623w	1143m	482w	515w
$Fe(L^2-L^2)$	3417s	1378vs	-	1597vs	1167s	515m	655w
$Fe(L^3–L^3)$	3417m	1254m	1305m	1607s	1171m	435w	509s
$Fe(L^4-L^4)$	3408vs	1329s	-	1618s	1148m	479b	750m

b = broad, w = weak, sh = sharp, vs = very sharp, s = strong, m=medium

Table 2: Analytical data and some physical properties of the schiff base ligands and their metal (III) complexes.

Compounc	Moleculaformul (molar mass)	Colour	Melting point (^{0}C)	Yield(g (%)	Molar conductivity Scm^2/mol	Microanalysi found (calculated)%			
						C	H	N	M
L^1	$C_{17}H_{13}NO_2$ (263)	Yellow	230	0.63 (80)	5.0 x 0^{-3}	78.82 (77.55)	4.81 (4.98)	5.32 (5.32)	-
L^2	$C_{17}H_{12}N_2O_3$ (292)	Blood red	100	0.65 (74)	3.0 x 10^{-3}	67.99 (69.86)	4.20 (4.10)	8.45 (9.58)	-
L^3	$C_{18}H_{15}NO_2$ (277)	Yellow	140	0.65 (78)	3.7 x 10^{-3}	76.02 (78.53)	5.53 (4.76)	5.17 (5.09)	
L^4	$C_{17}H_{13}NO$ (247)	Yellow	120	0.71 (97)	8.0 x 10^{-3}	70.02 (82.58)	5.63 (5.30)	5.19 (5.66)	-
Fe(L^1-L^1)	$Fe(C_{17}H_{10}NO_2)_2$ (581.85)	Dark brown	233	6.37 (98)	10 x 10^{-3}	73.66 (70.11)	4.58 (4.50)	5.14 (4.81)	9.04 (9.59)
Fe(L^2-L^2)	$Fe(C_{17}H_{10}N_2O_3)$ (639.85)	Black	249	6.80 (78)	3.0 x 10^{-3}	68.63 (63.77)	3.55 (3.78)	8.10 (8.74)	8.77 (8.72)
Fe(L^3-L^3)	$Fe(C_{18}H_{13}NO_2)_2$ (607.85)	Black	240	6.55 (86)	5.3 x 10^{-3}	75.54 (71.30)	5.16 (4.32)	5.24 (4.62)	9.23 (9.22)
Fe(L^4-L^4)	$Fe(C_{17}H_{11}NO)_2$ (549.85)	Dark green	160	6.15 (92)	7.0 x 10^{-3}	64.54 (74.19)	5.27 (4.76)	4.44 (5.09)	10.10 (10.20

L^1 – L^4 = Schiff base ligands. M =Fe(III)

Table 3: Electronic absorption spectra data for the Schiff base ligands and their metal (III) Complexes**.**

Ligands/Complexes	Absorbance(nm)	λ_{max}(cm^{-1})	Band assignment	Geometry
L^1	465	21,505	$n - \pi^*$	-
	448	22,321		
L^2	365	27,397	$\pi - \pi^*$	-
	311	32,154		
L^3	464	21,552	$n - \pi^*$	-
	446	22,421		
L^4	315	31,175	$\pi - \pi^*$	-
	229	43,668		
$Fe(L^1-L^1)$	309	32,362	$^6A_{1g}\rightarrow^4T_{2g}$	Octahedral
	448	22,321	$^6A_{1g}\rightarrow^4T_{1g}$	
	467	21,413	$^6A_{1g}\rightarrow^4T_{1g}$	
$Fe(L^2-L^2)$	315	31,746	MLCT	Octahedral
	357	28,011	$^6A_{1g}\rightarrow^4T_{2g}$	
	269	37,175	MLCT	
$Fe(L^3–L^3)$	445	22,472	$^6A_{2g}\rightarrow^4T_{1g}$	Octahedral
	462	46,851	$^6A_{1g}\rightarrow^4T_{1g}$	
	339	29,499	$^6A_{1g}\rightarrow^4T_{2g}$	
$Fe(L^4-L^4)$	438	22,831	$^6A_{2g}\rightarrow^4T_{1g}$	Octahedral
	457	21,881	$^6A_{2g}\rightarrow^4T_{2g}$	
	316	31,646	MLCT	

Where: M L C T = Metal ligand charge transfer, λ= maximum wave length of absorbance**.**

The ligands are all yellow in colour except L^2 which is dark red. The complexes have various shades of colours (Table1).The ligands and the complexes all have sharp melting points. The microanalysis results (C, H, N) are in close agreement to the calculated values. Molar conductance showed that the complexes are non-electrolytes. They have sharp melting points and are soluble or slightly soluble in the organic solvents used. The complexes are formed in a moderate yields ranging from 47-98%.

Infrared

In the Fe (III) complexes the υ (M-O) band were seen at 479 – 482 cm^{-1}. A weak band intensity [4].The stretching frequencies of the ligands was observed at 1612 – 1626 cm^{1} which are assigned to, υ(C=N). These were shifted to 1625 – 1576 cm^{-1} In the Fe (III) complexes, υ(C=N) bands shifted to 1623 – 1597 cm^{-1} In general the υ (C=N) bands observed in the ligands shifted to lower frequencies in the complexes. This indicates coordination of the metal ions to the azomethine nitrogen of the ligands [5]. In the Fe (III) complexes a band of υ(O-H) was observed at 3446cm^{-1}. The υ(C–O) (phenolic) In the Fe (III) complexes the bands shifted to a higher frequency of (1247 -1378 cm^{-1}).This is an indication of bonding through phenolic oxygen [7].

Electronic Spectra

The electronic spectra of the complexes revealed that the complexes have broad bands in the visible region which may be due to d – d transitions of the metal ions. However in the Fe(L^1-L^1) and Fe(L^3-L^3) complexes, bands observed at 32362, cm^{-1}and 29499 cm^{-1} were assigned to $^6A_{1g}\rightarrow{}^4T_{2g}$ transition [8]. Bands observed at 31746, 37175, and 31646 cm^{-1} were assigned to MLCT transitions in Fe(L^2-L^2) and Fe(L^4-L^4) .The bands observed at 21413 and 22321 cm^{-1} were assigned to $^6A_{1g}\rightarrow{}^4T_{1g}$ transition in Fe(L^1-L^1) .In the Fe(L^3-L^3) complex, the band observed at 22472 cm^{-1} was assigned to $^6A_{2g}\rightarrow{}^4T_{1g}$ transition [9]. Bands observed at 22831 cm^{-1} and 21881 cm^{-1} were also assigned to $^4A_{2g}\rightarrow{}^4T_{2g}$ transitions in Fe(L^4-L^4). The band observed at 46851 cm^{-1} was assigned to $^6A_{1g}\rightarrow{}^4T_{1g}$ transition in Fe(L^3-L^3) complex. The band observed at 28011 cm-^{1} was assigned to $^6A_{1g}\rightarrow{}^4T_{2g}$ transition in Fe(L^2-L^2) [9].

CONCLUSION

The schiff base ligands derived from 2-hydroxy -1- naphthaldehyde and their and Fe(III) complexes have been synthesized and characterized using elemental analyses, conductance measurements, UV/Visible and infrared studies. From the results obtained the ligands and their complexes have high melting points ranging from 100 ^{0}C to 252 ^{0}C. Molar conductivity of the complexes indicated that they are non-electrolytes. The ligands and their complexes show various colours ranging from yellow, green, brown, blood red and black. These are typical of transition metal complexes. The complexes are formed in moderate yields ranging from 47-98%. Infrared studies indicate that the schiff base ligands coordinated to the metal ions through the azomethine nitrogen and oxygen atom of the ligands. The electronic spectral results could not be used to confirm the geometries of the complexes as well defined bands were not observed in the visible region. However, the complexes are proposed to be six coordinated. This stoichiometry agrees with microanalysis results which reveals that all the complexes have 1:2 (metal : ligand) mole ratio. All complexes are stable at room temperature. It is also recommended that the further studies like acute, sub-acute and chronic toxicity test should also be carried out to know the level of safety of the complexes since complexes can be used in the production of dyes and drugs etc.

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