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**Cobalt (II), manganese (II) complexes with bidentate Schiff bases of benzhydrazide: Synthesis, characterization and electrochemical studies.**

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**Abstract**

The synthesis, characterization and cyclic voltammetry of some benzhydrazide Schiff bases and their metal complexes are reported. The structures of the novel complexes were elucidated by means of FTIR, FT <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, elemental analyses, cyclic voltammetry studies and thermal gravimetric analyses. Tautomeric properties of the ligating Schiff bases were observed from the infrared and proton NMR data. The electrochemical parameters indicated quasi-reversible redox activity.

*Keywords:* benzhydrazide Schiff bases, cobalt(II) and manganese(II) complexes, and cyclic voltammetry.

**1.0 Introduction**

The important place held in coordination chemistry by cobalt(II) and manganese (II) complexes of Schiff base ligands is confirmed by the surveys which are continuously being made. Schiff bases of benzhydrazide are known to constitute an interesting ON bidentate ligand system. This work represents their coordination behaviour to the metal center through IR and NMR data. The thermal gravimetric analysis (TGA) will indicate the presence of either coordinated water or water outside the coordination sphere and the decomposition pattern of the ligands. The redox activity of the complexes will be studied by cyclic voltammetry technique.

**2.0 Materials and Methods**

The benzhydrazide Schiff base ligands, La, Lb, Lc and Ld were prepared by condensing the hydrazide with 2-hydroxyacetophenone (La), 5-chloro-2-hydroxyacetophenone (Lb), thiophene-2-carboxaldehyde (Lc) and 3-methylthiophene-2-carboxaldehyde (Ld). The ligands have been satisfactorily characterized by elemental analysis, IR, <sup>1</sup>H and <sup>13</sup>C NMR.

The cobalt(II) and manganese(II) of complexes of general formula M(L)<sub>2</sub>H<sub>2</sub>O were prepared by refluxing the metal acetate in the appropriate ligand in (1:2) molar proportion in medium yield (40-60 %) using absolute ethanol. All of these complexes are brown to black solids which are air and heat stable. They have rather low solubility in common

organic solvent but are quite soluble in DMF and DMSO. The electronic spectra and cyclic voltammetry were recorded in DMSO.

### 3.0 Results and Discussions

The elemental analysis for both ligand and complexes are summarized in the Table 1.0 and they are satisfactorily characterized to the proposed structure.

**Table 1 : Elemental analyses for the ligands and complexes [% , found (theory)]**

Compounds	C	H	N
La	71.46(70.85)	6.21(5.55)	11.35(11.02)
Lb	62.10(62.40)	3.35(4.54)	11.50(9.70)
Ld(H <sub>2</sub> O)	63.80(63.91)	4.82(4.95)	11.67(11.47)
Co(La) <sub>2</sub> (H <sub>2</sub> O)	65.33(63.49)	4.77(4.97)	11.71(9.87)
Co(Lb) <sub>2</sub>	57.41(56.62)	4.23(4.12)	10.28(8.81)
Mn(La) <sub>2</sub>	63.76(63.94)	4.71(5.01)	9.85(9.94)
Mn(Lb) <sub>2</sub> (H <sub>2</sub> O)	52.44(52.45)	1.94(4.08)	8.01(8.16)

### 3.1 Infra-Red Spectra

All the four ligands exhibit medium intensity of N-H band around 3200 cm<sup>-1</sup> (Table 2). The phenolic OH is observed at around 3060 cm<sup>-1</sup>. The strong bands, the C=O and the C=N are observed ca. 1650 and 1605 cm<sup>-1</sup> respectively.

**Table 2 : Selected IR bands for ligand and Complexes in cm<sup>-1</sup>**

Compounds	O-H of H <sub>2</sub> O	NH	Phenolic OH	C=O	C=N	C-O Phenol	(C-O) enol	M-O	M-N
La	-	3219	3070	1650	1607	1284	-	-	-
Lb	-	3240	3062	1646	1609	1288	-	-	-
Lc	-	3301	3073	1660	1641	1275	-	-	-
Ld	-	3227	3068	1648	1597	1290	-	-	-
Co(La) <sub>2</sub> (H <sub>2</sub> O)	3449	-	3066	-	1599	1235	1132	585	470
Co(Lb) <sub>2</sub>	3449	-	3066	-	1610	1277	1136	542	475
Co(Ld) <sub>2</sub>	3414	-	3065	-	1587	1258	1145	634	526
Mn(La) <sub>2</sub>	3430	-	3063	-	1595	1231	1140	592	437
Mn(Lb) <sub>2</sub> (H <sub>2</sub> O)	3435	-	3060	-	1579	1228	1133	679	457

The cobalt(II) and manganese(II) complexes display both OH due to coordinated H<sub>2</sub>O molecule and phenolic hydroxyl group. Both NH and the C=O groups disappear in the complexes which could be due to enolisation of the benzhydrazide Schiff bases to the enolic form upon coordinating to the metal center[1]. The C=N band shifted to lower wave number indicating the formation cobalt(II) and manganese(II) complexes via C=N as well as C=O group. Two new bands at ~ 590 and in the 470-526 region are due to the M-O and

M-N bond respectively. The data confirm the formation of the cobalt(II) and manganese(II) complexes.

### 3.2 $^1\text{H}$ and $^{13}\text{C}$ NMR Studies

$^1\text{H}$  and  $^{13}\text{C}$  NMR Studies for both ligands and the cobalt complexes only are summarized in Table 3.0. The OH-proton signal corresponds to the uncoordinated of the ligand. The  $\text{N}_\text{H}$  proton signal of the ligands and cobalt complexes are observed in 10.76 to 11.73 ppm region.

**Table 3:  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR for ligand and Complexes ( ?, ppm)**

Compounds	$^1\text{H}$			$^{13}\text{C}\{^1\text{H}\}$			
	O-H	N-H	CH <sub>3</sub>	C=O	C=N	C-OH	CH <sub>3</sub>
La	13.39	11.38	2.49	164.75	18.46	158.81	14.17
Lb	13.46	11.46	2.49	164.70	156.89	157.52	14.26
Lc	-	10.76	2.35	163.60	152.80	-	15.10
Ld(H <sub>2</sub> O)	-	11.73	2.31	162.73	140.01	-	13.57
Co(La) <sub>2</sub> (H <sub>2</sub> O)	-	-	3.29	172.36	164.12	156.31	15.92
Co(Lb) <sub>2</sub>	13.40	11.41	3.21	173.35	163.27	155.17	16.20

Coordination of C=O and the azomethine nitrogen to the metal center are reflected in the downfield shift of these groups. In cobalt(II) complexes with La and Lb Schiff bases, the involvement of the azomethine nitrogen is indicated by the shift of the -CH<sub>3</sub> proton signals from 2.49 to 3.25 ppm. This is confirmed by downfield shift of the methyl carbon in  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra from ~14 ppm to ~15 ppm.

Both the IR and NMR data have indicated that the benzhydrazide Schiff base ligands are coordinated to the metal center in two ways, thus representing these ligands to act as bidentate ligands.

### 3.3 Thermogravimetric Analysis (TGA)

The TGA curves for all the complexes are thermally stable around 180°C. The thermal decomposition of complexes with coordinated water occurs in five steps while those without it occur in four steps only. The TGA curves for the two types of complexes are given in Figures 1 and 2 and the analysis are summarized in Tables 4 and 5. The first decomposition step between 180-280°C is attributed to the loss of one water molecule. The data is consistent with the results reported in IR. Thereafter, the decomposition of the two ligands took place one after another continuously up to ca. 780°C giving metal oxide as residue.

Fig. 1.0: TGA Curve for Co(Lb)<sub>2</sub>

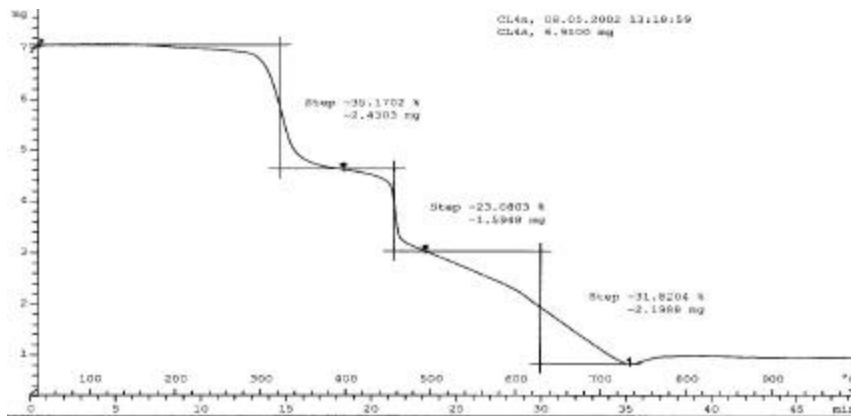
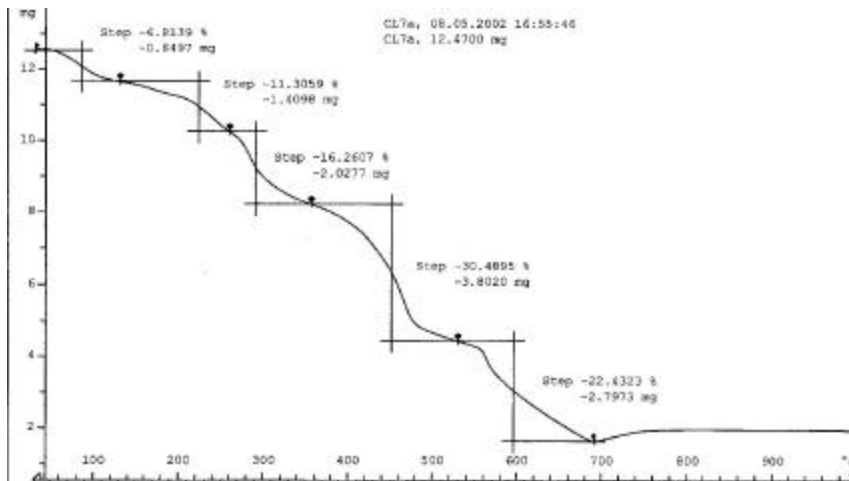


Table 4: TGA data for Co(Lb)<sub>2</sub>

Step	% Found	% Calculated	Group losses
1	35.18	35.17	2[C <sub>7</sub> H <sub>5</sub> N]
2	24.04	23.08	2Cl + CH <sub>3</sub> C=N
3	31.42	31.82	C <sub>6</sub> H <sub>6</sub> O
4	11.77	9.93	C-O

Fig. 2.0: TGA curve for Co(La)<sub>2</sub>(H<sub>2</sub>O)



**Table 5: TGA data for Co(La)<sub>2</sub>(H<sub>2</sub>O)**

Step	% Found	% Calculated	Group losses
1	5.98	5.02	Non - coordinated H <sub>2</sub> O
2	15.13	14.51	Coord. H <sub>2</sub> O + N=CMe + 4H (from OH)
3	45.37	46.86	C <sub>11</sub> H <sub>6</sub> NO
4	27.69	27.89	C <sub>6</sub> H <sub>4</sub> O + O
5	5.83	10.45	Co - O

### 3.4 Cyclic voltammetry

Cyclic voltammetry of cobalt(II) and manganese(II) complexes at a platinum electrode were recorded in DMSO containing 0.1M tetrabutyl ammonium tetrafluoroborate as supporting electrolyte.

**Table 6 : Cyclic voltammetry data for the complexes**

Complexes	Oxidation E <sub>a</sub> (mV)	Reduction E <sub>c</sub> (mV)	E (mV)	I <sub>a</sub> (? A)	I <sub>c</sub> (? A)	I <sub>a</sub> /I <sub>c</sub>
Co(La) <sub>2</sub> (H <sub>2</sub> O)	-699	-759	60	2.0	3.8	0.5
Co(Lb) <sub>2</sub>	-734	-779	45	1.07	1.6	0.7
Mn(La) <sub>2</sub>	-755	-802	27	0.8	1.4	0.6

The numerical data are given in Table 6.0 (only three complexes were obtained the electrochemistry data). Cathodic and anodic peaks of cobalt complexes with ligand La and Lb are in the 60 - 45 mV range at a scan rate of -10 mV/sec indicating one electron transfer in the redox activity while the complex Mn(La)<sub>2</sub> could involve more than one electron oxidation. All the complexes are quasi-reversible redox activity as shown from their I<sub>a</sub>/I<sub>c</sub> ratio data [2].

### 4.0 Conclusions

The IR and NMR studies have confirmed that the benzhydrazide Schiff bases act as bidentate ligand and coordinate to cobalt(II) and manganese(II) through the enolic form. The electrochemistry studies of both cobalt(II) and manganese(II) complexes have shown that they are of quasi-reversible redox activity [3]. The TGA and the elemental analysis data have indicated the presence of coordinated water as well as water outside the coordination sphere of the complexes. The proposed structure of the complexes with coordinated water is a stable five-coordinate compound while without water, it would be cobalt(II) with two bidentate ligands only [4].

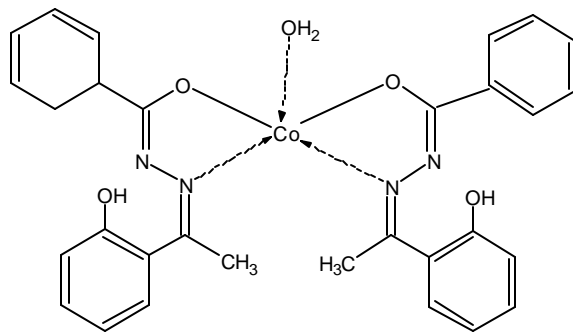


Fig 3.0: The proposed structure of the complex  $\text{Co(La)}_2(\text{H}_2\text{O})$ .

### 5.0 Acknowledgements

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### 6.0 References

1. S.M. Rahuma, S.O. Sharifah Rohaiza, M.A. Hapipah, and B. Wan Jeffrey, Vote-F Proceeding 2003, UM.
2. R. Greef, R. Peat, L.M. Peter, D. Pletcher and J. Robinson, Instrumental Methods In Electrochemistry, 1993, pg 189-190.
3. R.A. Cotton, G. Wilkinson CA. Murillo and M. Bochmann, Advanced Inorganic Chemistry 6<sup>th</sup> Edition., 1999, Pg. 5.
4. S.M. Rahuma, PhD Thesis, 2003, UM.