Research Journal of Chemical Sciences _____ ISSN 2231-606X
Vol. **3(9),** 69-76, September **(2013)** *Res. J. Chem. Sci.*

Microwave Assisted Synthesis and Characterisation of Diamagnetic Complexes

Jeeva J.* and Ramachandramoorthy T.
PG & Research Department of Chemistry, Bishop Heber College (Autonomous), Tiruchirappalli – 620 017, Tamilnadu, INDIA

Available online at: www.isca.in
Received 28th August 2013, revised 10th September 2013, accepted 16th September 2013

Abstract

New Cadmium and Mercury complexes with mixed ligands 4-hydroxypyridine and Cyanate ion were synthesised using microwave field. These complexes were characterized by analytical and spectral studies. And also by electrochemical and thermal behavior, the formulae and the geometry of the complexes were confirmed.

Keywords: Infrared, electrochemical, thermogram, microwave.

Introduction

Cadmium and Mercury complexes have wide range of Industrial and Bioactivities[1]. From paints to pharmaceutical and from thermometer to dental chemistry both cadmium and mercury complexes are largely used[2]. Some of these complexes were prepared using microwave field using domestic microwave oven[3]. By microwave field, the complexes were prepared in few minutes with moderately high yield, and of pure product[4]. Here complexes are prepared using MW field and thus prepared complexes are characterized by elemental analysis, metal estimation, electrical conductance, IR, UV-visible and NMR spectra. Finally cyclic electrochemical and thermal studies are carried out to derive the formulae and geometry of the complexes.

Material and Methods

Metal nitrate and metal chloride are of AnalaR grade. The solvents viz., DMSO, acetonitrile, DMF, methanol, ethanol used are also of AnalaR grade and used as such. 4-hydroxypyridine was purchased from Alfa Aesar company.

Instrumental Analysis: For elemental analysis Elementar Vario EL III was used. Metal estimation for cadmium was done volumetrically and for mercury gravimetrically. Electrical conductivity measurements were carried out in acetonitrile medium (10^{-3}M) at 30^0C and was determined using a digital conductivity bridge (Equiptronics, EQ 660). The magnetic susceptibility measurements were done by Lakeshore VSM-7410. IR spectra were recorded using Perkin Elmer Spectrum RXI in 4000-400cm^{-1} range with KBr pellet technique. The cyclic voltammetric measurement was done by Princetone applied research, model –versa stat mc. ^{1}H NMR and ^{13}C NMR spectra were recorded in DMSO using Bruker AV III 500 MHz FT NMR spectrometer (TMS as internal standard reference). Thermal analysis was done in Perkin Elmer, Diamond TGA / DTA instrument.

Synthesis of Complexes: The mixture of cadmium nitrate and mercuric chloride in methanol of about lg each (3.22 mmol and 3.64 mmol respectively) with 4-hydroxypyridine 0.61g and 0.69g (6.42 mmol and 7.26mmol respectively) was irradiated in a microwaveoven for 10 seconds. Then sodium cyanate to the value of 0.42g and 0.47g (6.46 mmol and 7.23 mmol respectively) in ethanol medium was added with the resultant and the whole mixture was irradiated for about 10 seconds. The complexes precipitated were filtred, washed with ethanol and dried and kept in air tight container.

Results and Discussion

From elemental analysis, metal estimation and electrical conductance values of the complexes were found to be non electrolytes[5]. The electrical conductance values along with elemental analysis and percentage yield are given in table-1.

Infrared Spectra: Only important vibrational frequencies of 4-HP and OCN ion and its cadmium and mercury complexes have been collected.

The –OH absorption frequency for 4-HP is at 3425 cm^{-1}. This value is shifted to 3463 cm^{-1} and 3444 cm^{-1} in cadmium and mercury complexes respectively [6-8]. The C-H aromatic ring stretching frequency is at 2932 cm^{-1} for 4-HP and it is shifted to 2957 cm^{-1} and 2993 cm^{-1} respectively for cadmium and mercury complexes. The C$^{\cdots}$ N frequency for 4-HP is 1377 cm^{-1} is also shifted to 1403 cm^{-1} and 1394 cm^{-1} respectively in cadmium and mercury complexes. This shift in the corresponding values confirms the ligand 4-HP binding to their corresponding metal centers.

The symmetric stretching frequency of OCN^{-1} ion is at 1255 cm^{-1}. This on complexation with cadmium and mercury shifts to 1275 cm-1 and 1260 cm^{-1} respectively. The asymmetric stretching frequency of OCN^{-1} ion is at 2220 cm^{-1} which also shift to lower frequency at 1980 cm^{-1} and 2105 cm^{-1} in cadmium

and mercury complexes which further confirms the ligand entry into the co-ordination sphere (table-2, figure-1, figure-2).

Electronic Spectra: The electronic configuration of Cd(II) and Hg(II) complexes is d^{10}, which confirms the absence of any d-d transitions. But the blue shift absorption band in their spectra is suffered by Hypo or Hyper chromic effect[9,10]. They exhibit charge transfer transition at 300 nm and 301 nm respectively resulting in pseudotetrahedral geometry (table-3, figure-3, figure-4).

^{1}H NMR Spectra: For 4-HP the δ value for phonolic OH, aromatic H and H-C=N are δ 8.9, δ 7.3 and δ 2.5 respectively and these values show a shift in cadmium and mercury complexes, thus confirming the ligand 4-HP entry into the coordination sphere[11] (table-4, figure-5).

^{13}C NMR SPECTRA: The shift in the values of 4-HP and OCN in complexes with respect to free ligand well proves its coordination to metal centers[12]. The values of the signal are shown in table-5, figure-6.

Electrochemical Behavior: The electrochemical properties of complexes in solution are studied by cyclic voltammetric technique[13]. The voltammograms of complexes are obtained in acetonitrile solution on platinum electrode with a scan rate of 0.5V/s. Cadmium and mercury complexes are involved in reversible electrochemical process at the voltage range of (-0.97) – (-1.09) V and (-0.69) – (-0.92) V respectively. Anodic oxidation of these complexes are oxidized in more positive values[14] figure-7.

Thermal Analysis: Thermograms are recorded in nitrogen temperature with 200ml per minute at a heating rate of 10^0C per minute. Thermogram of cadmium and mercury complexes indicate the total weight loss of about 98% around 725^0C. which is observed in three steps. A small weight loss at 120^0C – 170^0C was 8.8% which is assigned to the loss of OCN to form CO_2. Secondly, weight loss in the range 330^0C -395^0C was 17.6% which corresponds to the loss of one mole of 4-HP. The third weight loss in the range 490^0C to 551^0C with 23% was due to the loss of another one mole of 4-HP. And a small exothermic reaction at 605^0C -630^0C was noticed and this may be due to the nitrogen in OCN and 4-HP which form NO_2. Above this temperature metal oxide is formed[15-17]. Similar result occurs for mercury complex (table-6, figure-8).

Table-1
Analytical data of the complexes

S. No.	Complex	Colour	Yield %	Elemental Analysis				Electrical Conductance Ohm^{-1} cm^2 mol^{-1}
				C%	H%	N%	Metal%	
1.	$[Cd(4\text{-}HP)_2(0CN)_2]$	Pale Brown	81.9	(37.25) (37.27)	(2.58) (2.60)	(14.47) (14.49)	(26.82) (26.84)	72.6
2.	$[Hg(4\text{-}HP)_2(OCN)_2]$	Colourless	50.7	(30.35) (30.37)	(2.10) (2.12)	(11.77) (11.79)	(39.54) (39.56)	76.4

(Theoretical values are given in parenthesis)

Table-2
IR spectral data of 4-HP and cyanate ion complexes (cm^{-1})

S. No	Compound	-OH	C-H Aromatic	C⁻⁻⁻N	(OCN) Symmetric Stretching	(OCN) Asymmetric Stretching
1.	4-HP	3425	2932	1377	-	-
2.	$[Cd(4\text{-}HP)_2\ (OCN)_2]$	3463	2957	1403	1275	1980
3.	$[Hg(4\text{-}HP)_2\ (OCN)_2]$	3444	2993	1394	1260	2105

Table-3
UV-Visible spectral data of 4-HP and cyanate ion complexes (nm)

S. No	Compound	λ max (nm)	Assignment	Probable Geometry
1.	$[Cd(4\text{-}HP)_2\ (OCN)_2]$	300	Charge transfer	Pseudotetrahedral
2.	$[Hg(4\text{-}HP)_2\ (OCN)_2]$	301	Charge transfer	Pseudotetrahedral

Table-4
^{1}H NMR spectral data of compounds (δ)

S. No	Compound	Phonolic -OH	Aromatic –H	H- C⁻⁻⁻N
1.	4-HP	8.9	7.3	2.5
2.	$[Cd(4\text{-}HP)_2\ (OCN)_2]$	7.7	6.8	2.5
3.	$[Hg(4\text{-}HP)_2\ (OCN)_2]$	7.7	6.2	2.5

Table-5
^{13}C NMR Spectral data of compounds (ppm)

S. No	Compound	Aromatic Carbon	C···N	C-OH
1.	4-HP	120	140	155
2.	$[Cd(4\text{-}HP)_2(OCN)_2]$	117	143	155
3.	$[Hg(4\text{-}HP)_2(OCN)_2]$	116	142	155

Table-6
Thermal analysis data of cadmium complex

S. No	Complex	Type of degradation	Temperature		% Degradation	Possible Species Evolved
			Start^{0}C	End^{0}C		
1.	$[Cd(4\text{-}HP)_2(OCN)_2]$	Endothermic reaction	120^{0}C 330^{0}C 490^{0}C	170^{0}C 395^{0}C 551^{0}C	8.8 17.6 23.0	Two moles of (OCN) One mole of 4-HP Another mole of 4-HP
		Exothermic Reaction	605^{0}C	630^{0}C		Nitrogen explode With oxygen
		Endothermic Reaction	Above	630^{0}C		Metal oxide

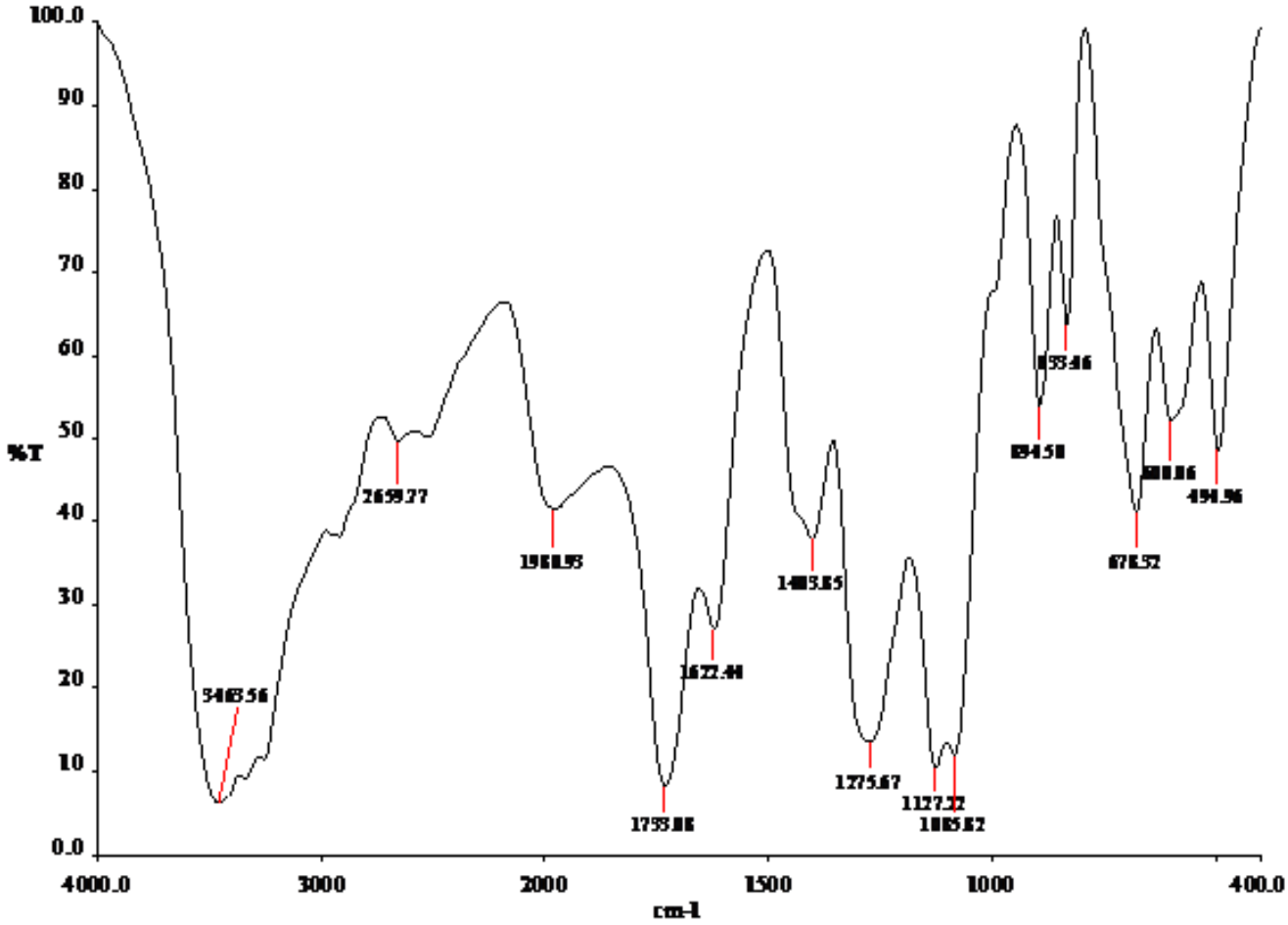

Figure-1
IR Spectrum of Cadmium complex

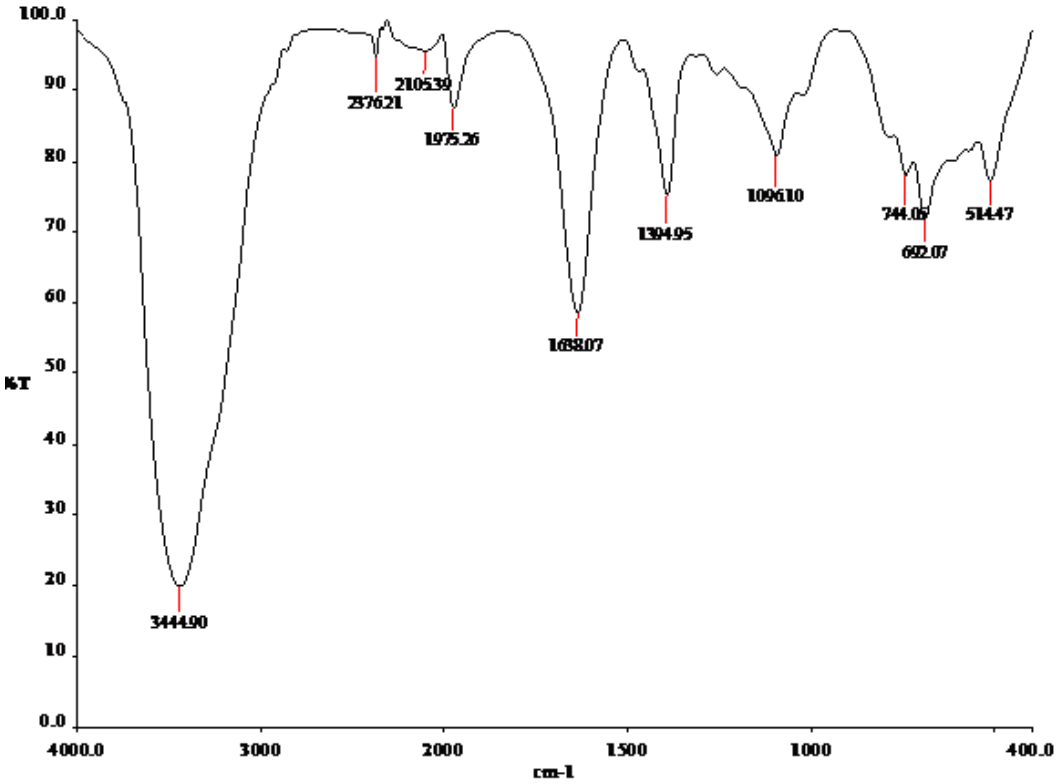

Figure-2
IR Spectrum of Mercury complex

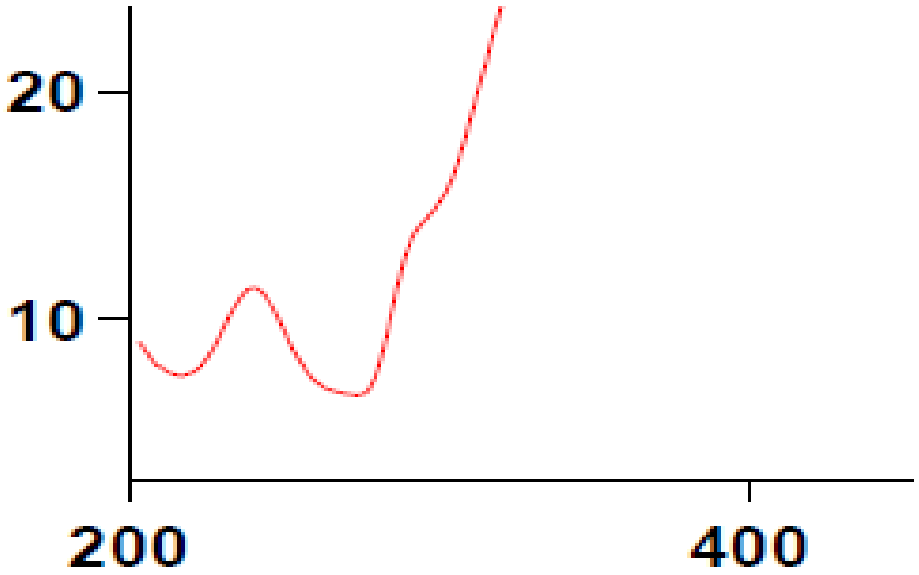

Figure-3
UV Spectrum of Cadmium complex (%R Vs Wavelength (nm))

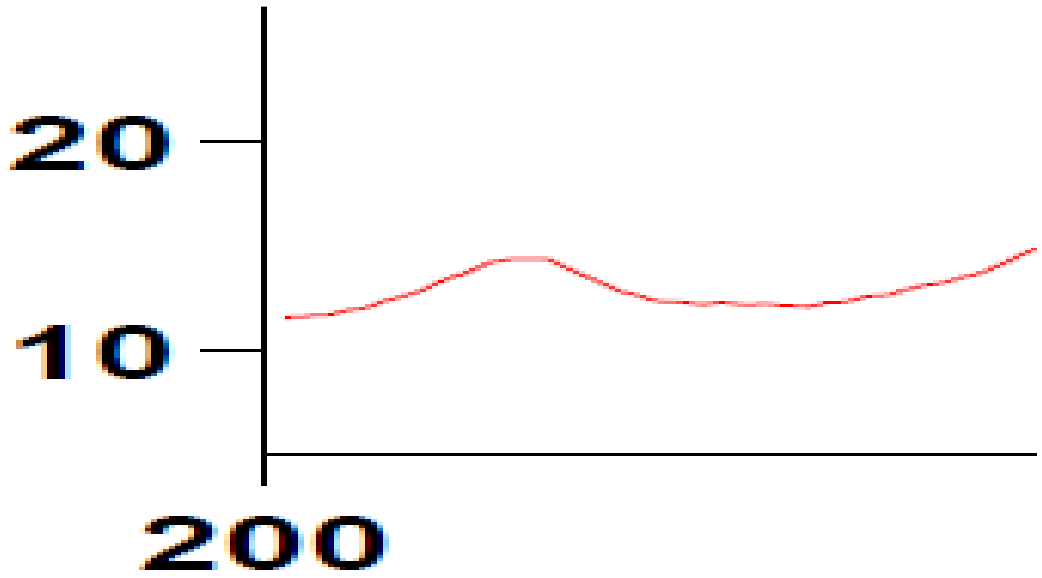

Figure-4
UV Spectrum of Mercury complex (%R Vs Wavelength (nm))

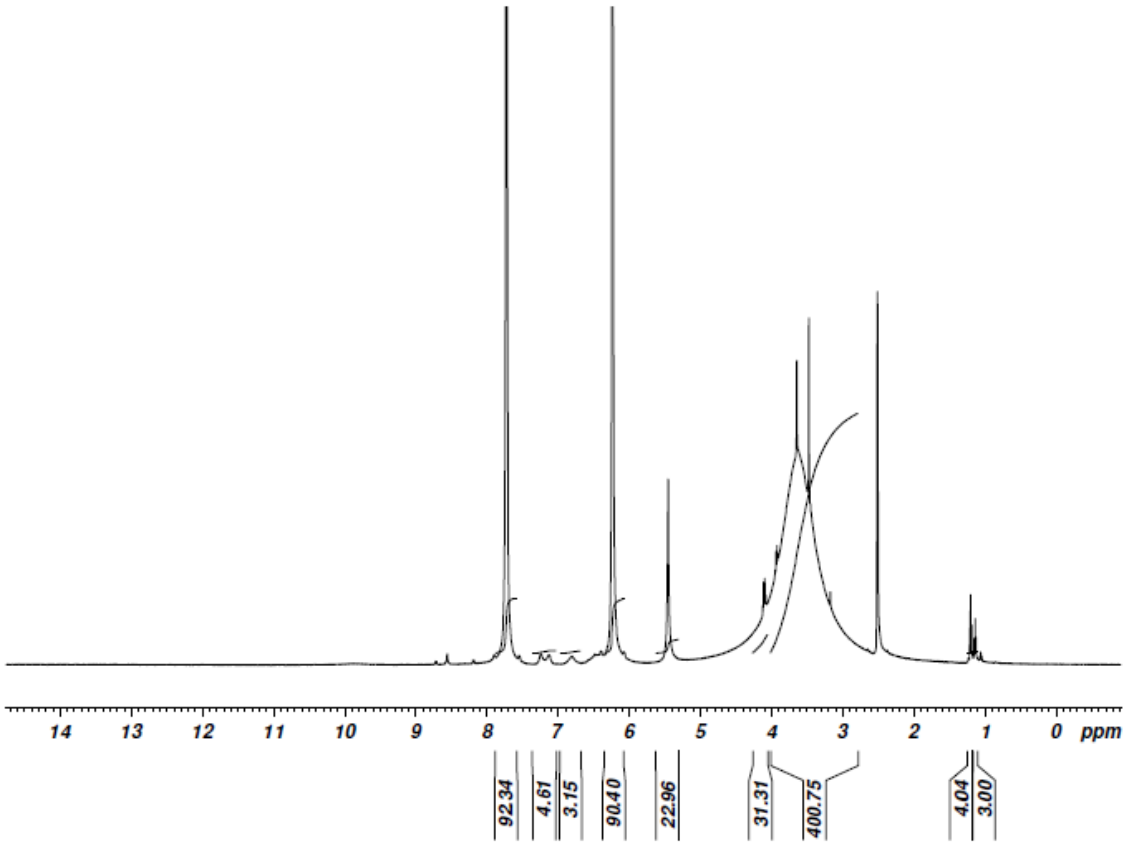

Figure-5
^{1}H NMR Spectrum of Mercury complex

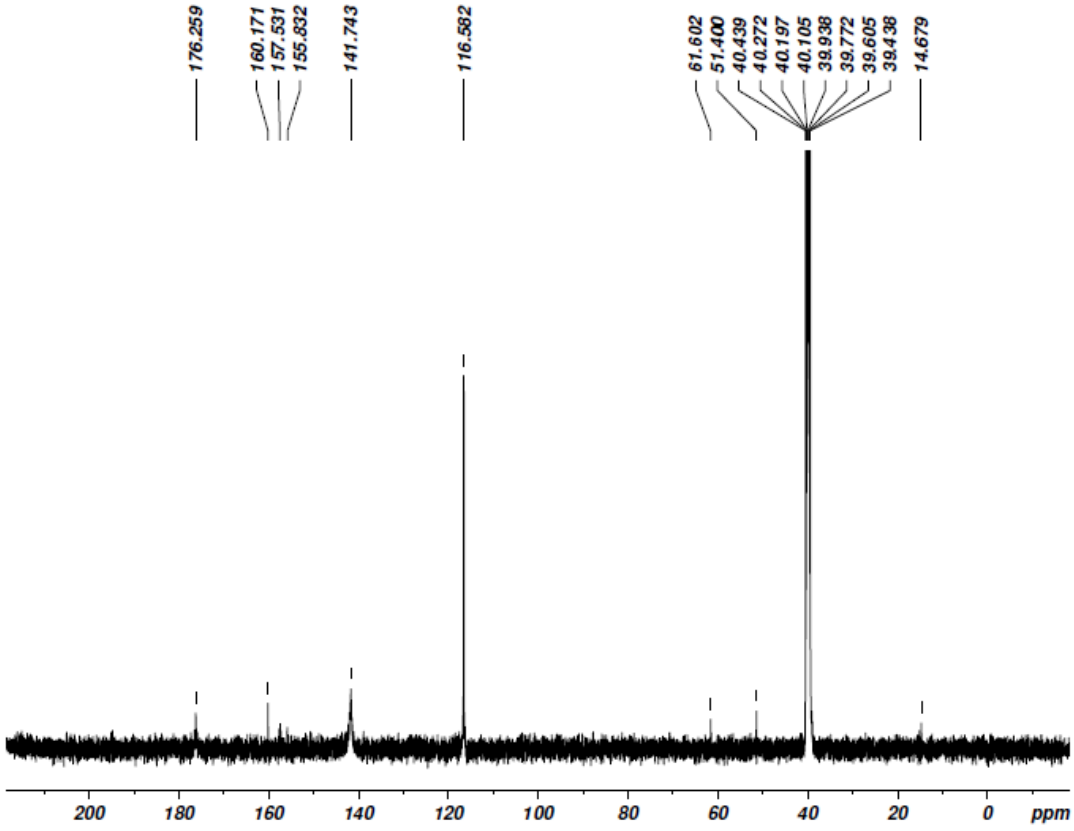

Figure-6
^{13}C NMR Spectrum of Mercury complex

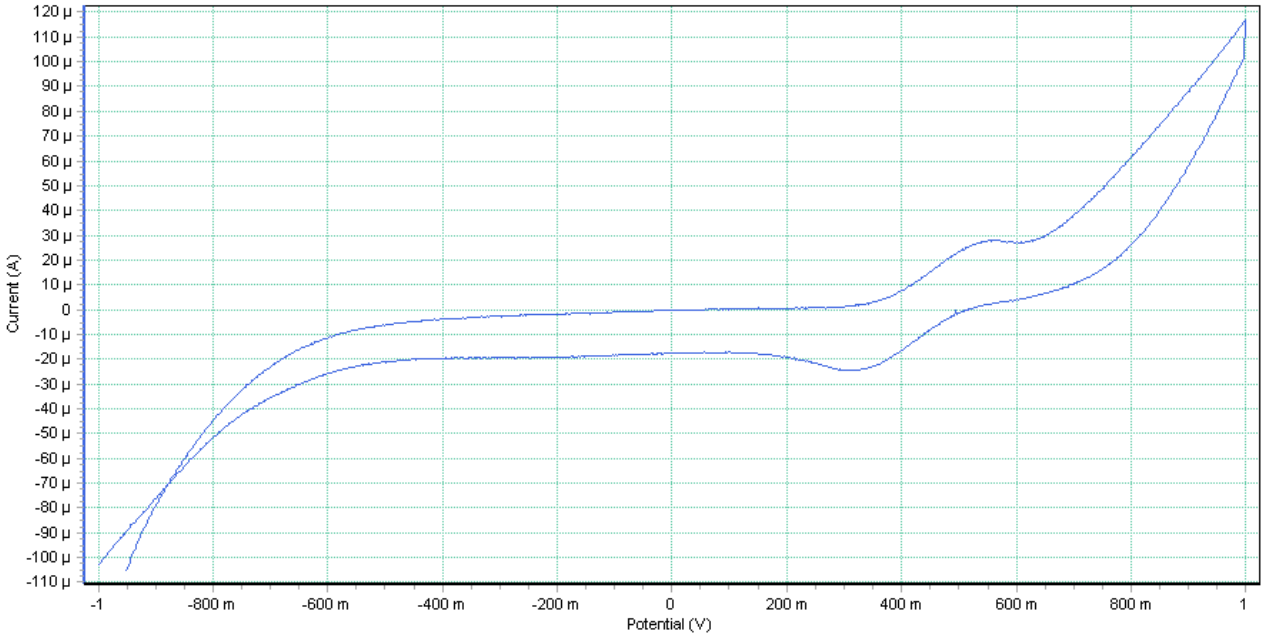

Figure-7
Cyclic voltammogram of cadmium complex

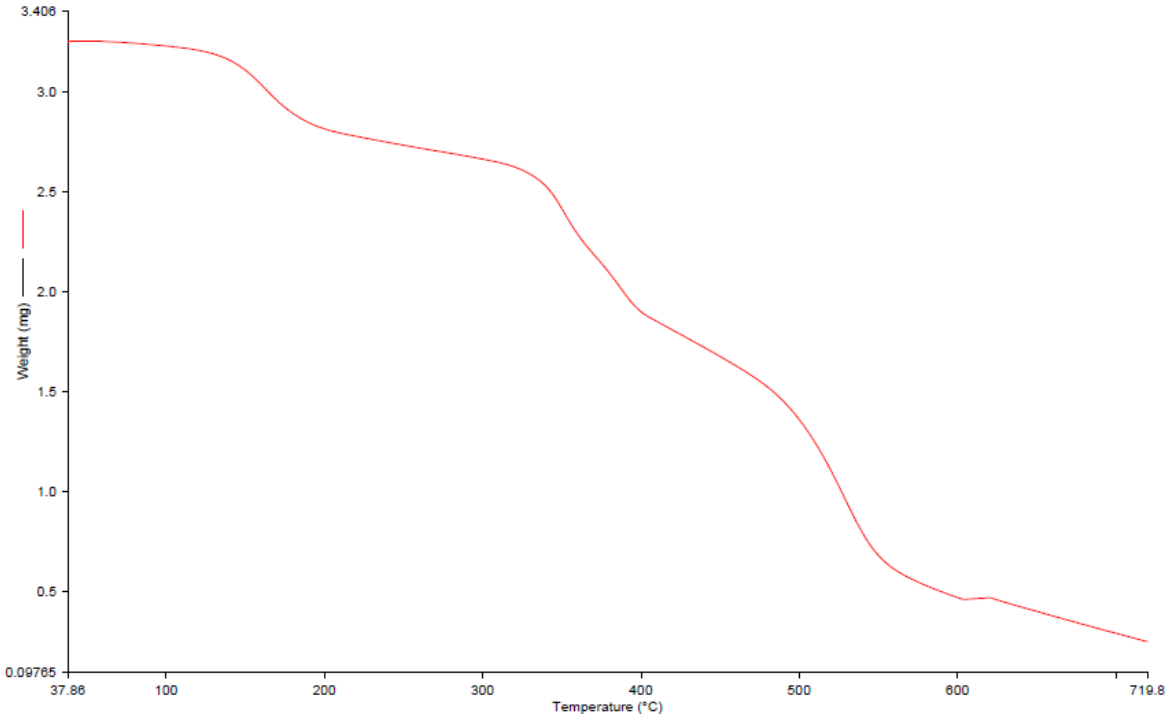

Figure-8
Thermogram of Cadmium complex

Conclusion

Complexes of cadmium and mercury with 4-hydroxypyridine and cyanate ion were synthesized and from their analytical and spectral studies along with electrochemical and thermal studies their formulae were confirmed as $[Cd(4\text{-}HP)_2\ (OCN)_2]$ and $[Hg(4\text{-}HP)_2(OCN)_2]$ and they have pseudotetrahedral geometry.

Acknowledgement

Authors thank the Principal and the management of Bishop Heber College (Autonomous), Tiruchirappalli - 620 017, for providing all facilities for the research work. And extend their thanks to SJC(ACIC)-Trichy, SAIF-Chennai and Mumbai and STIC-Cochin for providing all required data.

References

1. Yogesh P. Patil, Sachin H. Pawar, Sharu Jadhav and Jitendra S. Kadu, Biochemistry of metal absorption in Human body: Reference to check impact of nano particles on human being, *Int. J. of Sci and Res Pubs*, **3(4), (2013)**

2. Colman J. and Hegedu L.S., Principles and Applications of Organotransition Metal Chemistry, University Science Book, California **(1980)**

3. Godbert N., Pugliese T., Aziello I., Bellusci A., Crispini A., Ghedini M., Efficient, ultrafast, microwave – assisted syntheses of cycloplatinated complexes, *European Journal of Inorganic Chemistry*, **(32)**, 5105-5111 **(2007)**

4. Elisabete C.B. Alagria, Luisam D.R.S., Martins Matti Haukka and Armando J.L. Pombeiro., Rhenium complexes of tris (pyrazolyl) methanes and sulfonate derivative, *Dalton Tran*, 4954–4961 **(2006)**

5. Geary W.J., The use of Conductivity Measurements in Organic solvents for the Characterization of Coordination Compounds, *Coordi. Chem. Rev.*, **7(1), (1997)**

6. Silverstein R.M., Bassler G.L. and Morrill T.C., Spectrometric Identification of Organic Compounds, **4th edn**, wiley, 166 **(1981)**

7. Nakamoto K., Infrared and Raman Spectra of Inorganic and Coordination Compounds, wiley, **3rd edn (1997)**

8. George Socrates, Infrared and Raman Characteristic Group frequencies Tables and Charts, John wiley & sons, 18 **(2004)**

9. Lever A.B.P., Inorganic Electronic Spectroscopy, **2nd edn.**, Elsevier, **(1984)**

10. Cotton F.A. and Wilkinson G., Advanced Inorganic Chemistry, **5th edn**, Wiley, New York **(1988)**

11. Gupta Y.K., Agarwal S.C., Madnawat S.P. and Ramnarain., Synthesis, Characterization and Antimicrobial studies of some Transition metal complexes of Schiff Bases, *Res. J. Chem. Sci.,* **2(4)**, 68-71 **(2012)**

12. Balc, M., Basic P^1sH and p^{13}s - NMR spectroscopy, **Ist edn.**, Elsevier, pxii, 427 **(2005)**

13. Bagihalli G.B., Patil S.A. and Badami P.S., Synthesis, Physicochemical Investigation and Biological studies of zinc(II) complexes with 1,2,4-Triazole Schiff Bases, *J. of Ira. Chem. Soc*., **6(2)**, 259-270 **(2009)**

14. Neves E.A., De Andrade J.F and Chierice G.O., Anal. Chim. Acta, 155, 269 **(1983)**

15. Chaudhary Rakhi and Shelly, Synthesis, Spectral and Pharmacological Study of Cu(II), Ni(II) and Co(II) Coordination Complexes, *Res. J. of Chem. Sci.*, **1(5),** 1-5 **(2011)**

16. Chandran Ambily, Kuriakose Sunny and Mathew Tessymol, Synthesis, Characterization and Thermal Studies on natural polymers modified with 2-(5-(4-dimethylamino-benzylidin)-4-oxo-2-thioxo-thiazolidin-3-yl) acetic acid, *Res. J. of Chem. Sci.,* **2(12),** 37-45 **(2012)**

17. Break L.M. and Mosselhi M.A.N., Synthesis, Structure and Antimicrobial Activities of new 3- and 2-arylmethyl and arylacyl 3-H[1,2,4]triazino[3,2-6]quinazline-2,6(1H)diones, *Res. J. of Chem. Sci.*, **2(5),** 23-28 **(2012)**