

## **PREPARATION AND CHARACTERIZATION OF TOXIC METAL COMPLEXES OF NICOTINAMIDE AND NICOTINIC ACID**

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### **ABSTRACT**

Cd(II), Hg(II) and Pb(II) were reacted with nicotinamide and nicotinic acid (vitamin B<sub>3</sub>) in the aqueous medium. The solid products obtained were formulated by comparing the experimental and calculated data for C, H, N and metal. Both produce 2:1 compounds with the metal ions. The prepared complexes were characterized by different physicochemical methods. The UV-vis, FTIR spectral analysis, TG analysis of these complexes have been discussed. The conductance behavior of the complexes indicates that all of them behave as weak electrolytes.

Key words: Toxic metals, Nicotinamide, Nicotinic acid

### **INTRODUCTION**

Metal ions are very important for all living system and play very significant role in biological systems as micronutrients. Metal ions are very essential component of different organs of animals such as blood, bones, teeth, nerves, some proteins and enzymes. In the living bodies metals are mostly coordinated to other chemical species in it (Garret *et al.* 1968). The world is now facing the serious problem of environmental pollution. The toxic metals such as Pb, Cd, As, Hg, etc. are incorporated into drinking water and various food chains through biogeochemical cyclic processes (Lobinski 1997). Toxic metals are generally more important than abundant metals, in terms of environmental pollutant because of their effects on living organisms (Lehninger 1990) as toxic metals are not metabolized in the body and accumulate in the soft tissues (Schroeder 1975).

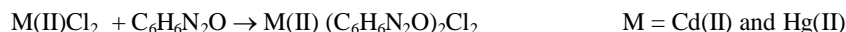
Vitamins are accessory dietary factors and are necessary in very small amount. Vitamins help the animal organism to perform some specific physiological functions and regulation of metabolic processes, which are vital to life (Lieberman and Bruning 1990, Claus and Taylor 1965). Niacin is one of the water soluble B-vitamins. In the blood, brain, kidney and liver it is converted to the coenzyme of nicotinamide. Tryptophan is an amino acid, which is a provitamin of niacin. We have been doing research on metal B vitamin complexes for few years (Ehsan *et al.* 2001, Shaikh *et al.* 2006 and Rahman *et al.* 2011). The present work includes the preparation of complexes of some toxic metal with nicotinamide and nicotinic acid in solid phase and their characterization using different conventional methods and studies of their various properties in order to establish the nature of metal-vitamin B<sub>3</sub> interactions.

## EXPERIMENTAL

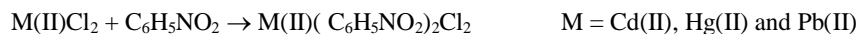
Analytical grade reagents (BDH, Aldrich and E. Merck) were used in this work. The melting points of the complexes were measured by STUART, Model SMP 11, VWR International Ltd. UK melting point apparatus with a capacity of recording the temperature up to 250°C. The metal content of the complexes were estimated using complexometric titration (Vogel 1989). Infrared spectra of all the compounds were recorded on a Fourier Transform IR Spectrophotometer (IR-Prestige-21, Shimadzu Corporation, Japan) in the range 400-4000 cm<sup>-1</sup> as KBr pellets. The electronic spectra of the ligands and their complexes with metals were recorded on a UV-Visible spectrophotometer, (UV-160A, Shimadzu Corporation, Japan), in the wave length range 200-800 nm. The thermogravimetric analysis (TGA) of the complexes were carried out with a computer controlled Thermo-Gravimetric Analyzer (TGA-50, Shimadzu Corporation, Japan). The conductivity of the complexes was measured with TOA conductivity Meter CM-55, made in Japan.

## PREPARATION OF THE COMPLEXES

*Metal-Nicotinamide complex:* 4 mmol metal salt, 8 mmol nicotinamide were dissolved in water separately. Then the solutions were mixed together with gentle stirring. White crystals formed immediately. The yield was 65-75 % on metal content. The compounds are stable in air and light. The compounds are soluble in hot water and hot ethanol. The reaction involved in the preparation may be written as below



*Metal -Nicotinic acid complex:* These complexes were prepared by reacting the ligand nicotinic acid and metal salts in 2:1 ratio. 4 mmol of metal salts and 8 mmol nicotinic acid were dissolved in water in separate beakers. Then the solutions were mixed together and gently heated. White crystals formed immediately after cooling. The yield was about 65 % on metal content. The compounds are soluble in hot water and hot ethanol, and stable in air and light. The reaction involved in the preparation may be written as below,



*Formulation of the complexes:* The formulation of the complexes was done by comparing the experimental microanalytical data of carbon, nitrogen, hydrogen and metal with that of calculated values and are tabulated in Table 1.

**Table 1: Percent composition of C, H, N and metal in the complexes**

Complex	Decomposition temp (°C)	% C		% H		% N		% M	
		Found	Cal.	Found	Cal.	Found	Cal.	Found	Cal.
Cd(C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub>	upto 250	33.78	33.70	2.76	2.83	13.03	13.11	25.2	26.29
Hg(C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub>	238 - 244	27.85	27.94	2.32	2.35	10.94	10.86	36.3	38.89
Cd(C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub>	198 - 220	33.70	33.55	2.29	2.35	6.53	6.52	24.9	26.17
Hg(C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub>	212 - 220	26.82	27.84	1.71	1.95	5.01	5.41	39.5	38.74
Pb(C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> ) <sub>2</sub>	upto 250	30.07	31.92	1.67	1.79	5.78	6.21	42.2	45.90

## RESULTS AND DISCUSSION

Complex compounds of niacinamide and niacinic acid with Cd(II), Hg(II), Pb(II), have been synthesized in aqueous medium. All the complexes were prepared following more or less same procedure and all appear to be white crystalline products. The closeness of the elemental analysis values with the calculated values indicate that the compounds are pure. The complexes are Cd(C<sub>6</sub>H<sub>6</sub>N<sub>2</sub>O)<sub>2</sub>Cl<sub>2</sub>, Hg(C<sub>6</sub>H<sub>6</sub>N<sub>2</sub>O)<sub>2</sub>Cl<sub>2</sub>, CdCl<sub>2</sub>.(C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>)<sub>2</sub>, HgCl<sub>2</sub>.(C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>)<sub>2</sub> and Pb(C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)<sub>2</sub>. The compounds decomposes at various temperature ranges (Table 1).

*IR spectral analysis:* The tentative assignments of the ir bands of the ligands and their metal complexes have been done on the basis of standard references (Dyke *et al.* 1978, Nakamoto 1978, Pavia *et al.*, 2001, and Rao 1963). The tentative assignments of the important ir bands of the ligands and the complexes are listed in Table 2 and 3.

*Complexes of Cd(II) and Hg(II) with Nicotinamide:* The pattern of ir spectra of the ligand and its complexes are more or less similar. Very small differences in peak positions are observed. The peaks of the complexes are sharper than those of the ligand. The N-H stretching vibrations of the ligand are observed at 3367 cm<sup>-1</sup> and 3170 cm<sup>-1</sup>, in the complexes the peaks appear at slightly higher field. In the Cd-nicotinamide complex the N-H stretching vibration appeared at 3420 cm<sup>-1</sup> and 3206 cm<sup>-1</sup> and in the Hg-nicotinamide complex the same peaks are observed at 3416 cm<sup>-1</sup> and 3327 cm<sup>-1</sup>. The CH absorption peaks are very weak in both ligand and the complexes. The N-H bending vibration in the ligand and the complexes appear in very narrow range, 1618 cm<sup>-1</sup> to 1623 cm<sup>-1</sup>. The ligand absorb broadly at 1680 and 1618 cm<sup>-1</sup> due to C=O and N-H bending mode of vibration. In this region the complexes absorb sharply for C=O, C=C and N-H stretching. The C-N stretching band appears near about 1400 cm<sup>-1</sup> in the ligand and the complexes. IR absorption frequencies for important functional groups of nicotinamide and its two complexes are compared in Table 2.

**Table 2: Important IR bands of nicotinamide and its complexes.**

Group frequency	C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O	Cd(C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub>	Hg(C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub>
N-H stretch	3367	3420	3416
	3170	3206	3327
C-H stretch	2830	2835	2832
C=O stretch	1680	1708	1664
N-H bend	1618	1670	1619
C=C stretch	1593	1623	1596
C-N stretch	1400	1400	1406

*Complexes of Cd(II), Hg(II) and Pb(II) with Nicotinic Acid:* The O-H stretching band is very broad and occurs at 3441 cm<sup>-1</sup> for ligand nicotinic acid. In Cd-nicotinic acid this broad band remains unchanged, in Hg-nicotinic acid the shape of the band changes and the intensity increases and appears at 3555 cm<sup>-1</sup> and in case of Pb-nicotinic acid the position of the band is unchanged but the intensity increases. The CH absorption peaks are very weak in ligand but in the complexes sharp peaks are obtained near 3000 cm<sup>-1</sup>.

The C=O stretching vibration appears as a broad band centered at 1706 cm<sup>-1</sup> in case of ligand. The C=O stretching vibration appears at 1696 cm<sup>-1</sup> in Cd-nicotinic acid complex, at 1711 cm<sup>-1</sup> in Hg-nicotinic acid complex and no peak was observed for Pb-nicotinic acid complex. In case of Pb complex two peaks appear at 1600 and 1392 cm<sup>-1</sup> due to asymmetric and symmetric stretching of carboxylate ion. IR absorption frequencies for important functional groups of nicotinic acid and its three complexes are compared in Table 3.

**Table 3: Important IR bands of nicotinic acid and its complexes.**

Group frequency	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	CdCl <sub>2</sub> .(C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> ) <sub>2</sub>	HgCl <sub>2</sub> .(C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> ) <sub>2</sub>	Pb(C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> ) <sub>2</sub>
O-H stretch	3441	3462	3555	3441
	2442	2570	2448	2445
C=O stretch	1706	1696	1711	1610
C=C stretch	1596	1600	1597	1392
C-O stretch	1301	1307	1303	1335

#### Ultraviolet-Visible Spectral Analysis

Ultraviolet-visible spectra are associated with a process of electronic transition. The energy of the electronic transition is quantized and is highly dependent on the electronic

structure of the molecule. The interpretation of absorption bands of the uv-visible spectra of the ligand and the metal complexes were done on the basis of standard references and previous papers (Silverstein *et al.* Lang 1961 and Gillam and Strem 1957). The tentative assignments of the bands are listed in Table 4.

The ligand nicotinamide showed two absorption bands at 207 nm and 259 nm. The first and second absorption bands are due to  $n \rightarrow \sigma^*$  and  $\pi \rightarrow \pi^*$  transition respectively. The  $n \rightarrow \sigma^*$  absorption band is due to the transition of nitrogen lone pair to the anti bonding orbital of C-N bond. The  $\pi \rightarrow \pi^*$  transition occurs either in C=N or in C=O or both, of the ligand molecule. The Cd and Hg complexes of the ligand nicotinamide absorbs identically at more or less same wave length, which indicate that the structure of the organic part of the complexes remain unchanged after the formation of complexes with metals.

Nicotinic acid also showed two absorption bands at 235.5 nm and 258 nm which are due to  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transition respectively. In the nicotinic acid molecule the  $n \rightarrow \sigma^*$  absorption band is due to the transition of oxygen lone pair to the anti bonding orbital of C-O bond. While  $\pi \rightarrow \pi^*$  transition occurs either in C=N or in C=O or both, as in the nicotinamide molecule.

**Table 4: UV- visible spectral data of ligands and different complexes**

Empirical formula of compounds	Absorption bands	
	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
$C_6H_6N_2O$	207	259
$Cd(C_6H_6N_2O)_2Cl_2$	207	258
$Hg(C_6H_6N_2O)_2Cl_2$	207	258
$C_6H_5NO_2$	235	258
$Cd(C_6H_5NO_2)_2Cl_2$	237.	259
$Hg(C_6H_5NO_2)_2Cl_2$	238	260
$Pb(C_6H_4NO_2)_2$	240	261

In this case also the complexes of nicotinic acid absorbs identically at more or less same wave length except the intensity of absorption, as the ligand, indicating that the structure of the organic part of the complexes remain unchanged after the formation of complexes with metals Cd, Hg and Pb.

#### *Conductivity Study*

To understand the ionic or covalent nature, the conductivity behavior of the solutions of different concentration of the complexes were studied. Since the compounds are

sparingly soluble in water or alcohols, conductance of the saturated solutions were measured first and then the conductance were measured by diluting the saturated solution to different extent such as 10 times, 20 times, 30 times and 40 times. The conductivity values of aqueous solutions of the complexes with concentration are listed in Table 5.

**Table 5: Conductance of different metal complexes**

Compound	Conductance of saturated solution ( $\times 10^6 S$ )	Conductance of different solution ( $\times 10^6 S$ )			
		Extent of dilution			
		10 times	20 times	30 times	40 times
KCl	287000	24200	18750	12540	9430
$Cd(C_6H_6N_2O)_2Cl_2$	864	75.8	57.3	39.1	29.7
$Hg(C_6H_6N_2O)_2Cl_2$	49.5	10.19	9.58	8.10	7.47
$Cd(C_6H_5NO_2)_2Cl_2$	1420	389	221	157.1	122.4
$Hg(C_6H_5NO_2)_2Cl_2$	77.5	30.9	25.1	19.12	17.3
$Pb(C_6H_4NO_2)_2$	327	50.7	29.9	21.6	16.54

The pattern of change of conductance value of the complexes with dilution is similar for all the complexes but the conductance values are different for different compounds. The conductance values of the complexes are very small compared to that of the strong electrolytes. So, on the basis of conductance values and pattern of conductance change with concentration we can say that all the complexes are weak electrolyte.

#### *Thermo Gravimetric Analysis (TGA)*

In the present study, the TGA of the complexes were conducted in a temperature controlled Thermo Gravimetric Analyzer. The thermograms of the ligand nicotinamide and its Cd-complexes are shown in Fig 1 and 2. The weight losses at different temperatures are recorded in Table 6.

The first weight-loss is about 2.32% for Cd-nicotinamide and 2.93% for Hg-nicotinamide compound may be due to the loss of adhered surface water. Therefore this strongly agree with the absence of any crystalline or coordinated water in the complexes. In case of Cd-nicotinamide 56.62% weight loss may be due to loss of some part of the organic component at around 400°C and at 600°C all the organic part of the molecule may be lost and the residue may be of the metal oxide. The weight loss 95.22% for Hg - nicotinamide occurred steeply in a short period of time around 300°C and it remained approximately constant until 600°C. The first weight-loss is about 1.92% for Cd-nicotinic

acid, 2.95% for Hg-nicotinic acid, 1.08% for Pb-nicotinic acid may be due to the loss of adhered surface water. Therefore this strongly agree with the absence of any chemically bound water i.e. chemically crystalline or coordinated water in the complexes. In Cd-nicotinic acid no valley was showed up and we may say that the final remaining weight may be due to the presence of metal oxide. In Hg-nicotinic acid complex 90.42% weight loss occurred steeply and in a short time and at 600°C only 2.40% weight remained. In case of Pb-nicotinic acid complex most of the weight remained and it suggests we needed to see the decomposition behavior in an extended temperature range.

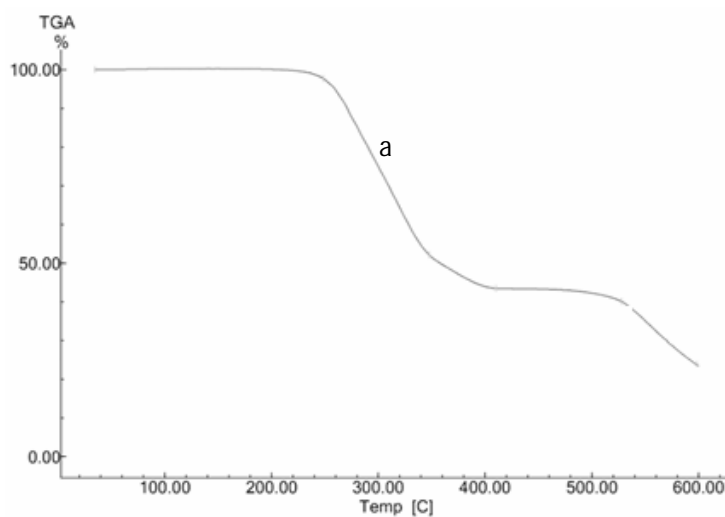


Fig. 1. Thermomogram of cadmium-nicotinamide complex.

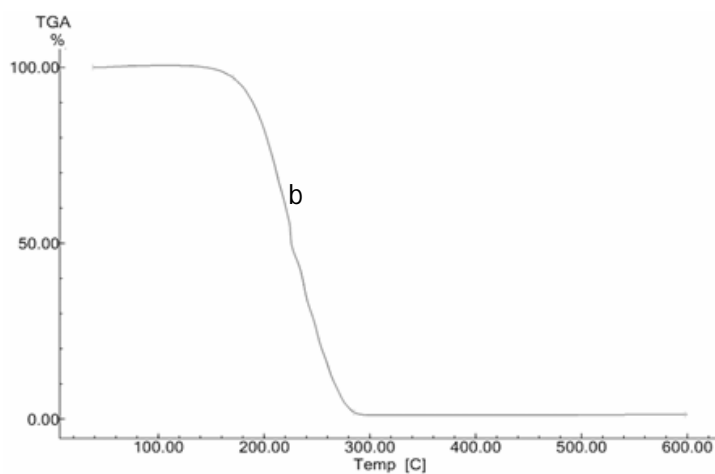


Fig. 2. Thermomogram of mercury-nicotinamide Complex

**Table 6: Weight loss recorded at different stages of TGA analysis of different complexes.**

Complex	Observed Temperature	% Weight lost	Probable Reasons
Cd(C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub>	248-410	47.92	CO <sub>2</sub> may be lost
	410-580	59.94	most of the organic part might be lost 23.69 % residue may be metal oxide
Hg(C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub>	200-300	98.15	No residue
Cd(C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub>	219-365	44.03	The complex might be decomposed
	365-600	35.58	most of the organic part might be lost
Hg(C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub>	190-310	97.6	No residue
Pb(C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> ) <sub>2</sub>	Room temp. -315	1.08	moisture loss
	315-427	30.26	organic part might be lost
	427-600	5.8	

## CONCLUSION

All the complexes prepared in the aqueous medium are stable crystalline powder. The ligand to metal ratio of the complexes is 2:1. They are weak electrolytes and soluble in hot water and hot ethanol.

The crystals of the compounds do not contain any chemically coordinated water which was confirmed by thermogravimetric analysis and ir spectral analysis.

The electronic absorption spectra of the complexes demonstrate that the bonding pattern is same in each complex of the same ligand.

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