



SPECTROSCOPIC CHARACTERIZATION AND THERMAL STUDIES OF NICOTINAMIDE ALKALINE EARTH METAL COMPLEXES

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ABSTRACT

Alkaline earth metal complexes of nicotinamide with general formula $[M(\text{nia})(\text{Cl})_2(\text{H}_2\text{O})_3]_n\text{H}_2\text{O}$ (where $M = \text{Mg(II)}, \text{Ca(II)}, \text{Sr(II)}$ and Ba(II) ; $n = 0-9$ water molecules) were obtained by the reactions of the corresponding metal chlorides with vitamin B3 (nia) in the presence of 1 : 4 (v : v) distilled water: methanol solvent at 70°C for about 30 min., and their suggested structures were determined by elemental analyses, molar conductivity, (infrared, UV-vis.) spectra, thermal analysis (TG), X-ray powder diffraction (XRD) as well as scanning electron microscopy (SEM). The results revealed that nicotinamide complexes associated with one of nia ligand coordinated toward metal ion to form six coordinated structures through N-bonded pyridine ligand. Antimicrobial were assessment against some kind of (G^+ and G^-) bacteria and fungi.

Key words: Vitamin B3, Nicotinamide, Alkaline earth metals, Spectral studies, Thermal studies.

INTRODUCTION

Heterocyclic compounds play an important role in many biological systems, especially N-donor ligand, which being a component of several vitamins and drugs¹⁻⁴. In biological system metal complexes of ligand, which has important biological effects are sometimes more effective than the free ligand⁵. Nicotinamide, also known as niacinamide is the amide of nicotinic acid (vitamin B3/niacin). Nicotinamide is a water soluble vitamin and is a part of vitamin B group. Niacin is converted to nicotinamide *in vivo*⁶. Nicotinamide is involved in electron transport phenomena in biological system⁷, and it combines with ribose, phosphoric acid and adenine to form two coenzymes. In addition, unicotinamide enhances cell replication in transplanted pancreatic islets^{8,9} and has anti-inflammatory properties. Deficiency of dietary niacin leads to pellagra, a human disease characterized by

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weakness, diarrhea, dermatitis and nervous disorders¹⁰. Magnesium and calcium are ubiquitous and essential to all known living organisms. They are involved in more than one role, with, for example Mg/Ca ion pumps playing a role in some cellular processes, magnesium functioning as the active center in some enzymes and calcium salt taking a structural role (e.g bones). Strontium and barium have a lower availability in the biosphere. Strontium plays an important role in marine aquatic life, especially hard corals. They use strontium to build their exoskeleton. These elements have some uses in medicine, for example "barium meals" in radio graphic imaging, whilst strontium compounds are employed in some toothpaste. Since the interaction of nicotinamide with transition metal elements is important for understanding the effect of it on vital organs, thus, a number of nicotinamide complexes and salt of nicotinamide have been investigated both structurally and spectroscopically¹¹⁻¹⁵. In addition of its biological activity, metal complexes of nicotinamide are important part of metal organic frame works, which are now considered for hydrogen storage applications¹⁶.

This paper is a continuation of our studies on complexes between some metals salts with dynamic pharmaceutical compounds which commonly used¹⁷. Nicotinamide complexes of Mg(II), Ca(II), Sr(II), Ba(II) have been synthesized and characterized elemental analysis, molar conductivity, (infrared, UV-vis) spectra, thermal analysis, X-ray powder diffraction as well as scanning electron microscopy. In addition, the *in vitro* antimicrobial and antitumor activities were assessment against some kind of (G^+ and G^-) bacteria and fungi (*Escherichia coli*, *staphylococcus Aureus*, *Bacillus subtilis* and *Pseudomouas aeruginosa*) and (*Aspergillus, flarus* and *candida Albicans*), respectively are reported.

EXPERIMENTAL

Chemicals

All chemicals (purity from 98-99%) were purchased and used without further purification. Nicotinamide (Fig. 1) was purchased from Fluka company and used without further purification. $MgCl_2 \cdot 6H_2O$, $CaCl_2$, $SrCl_2 \cdot 6H_2O$, $BaCl_2 \cdot 2H_2O$ were obtained from Aldrich company. All of the other reagents and solvents were purchased from commercial sources and were of analytical grade.

Synthesis of nia complexes

A solution of 8 mmol of each $MgCl_2 \cdot 6H_2O$, $CaCl_2$, $SrCl_2 \cdot 6H_2O$, $BaCl_2 \cdot 2H_2O$ in bi-distilled water (10 mL) was added dropwise to stirred solution of nicotinamide (8 mmol) in methanol (40 mL). The resulting solutions were stirred for 1 h, with heating at 70°C, the volumes of both solutions were reduced to 10 mL, leading to isolation of solid products,

which was left overnight till precipitated, washed with methanol and diethyl ether then finally dried under vacuum over anhydrous calcium chloride.

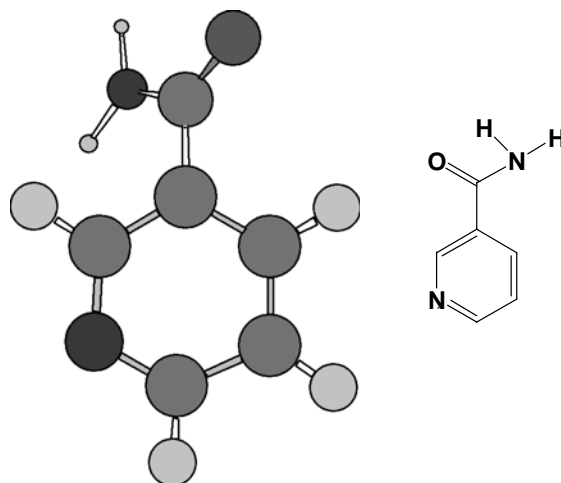


Fig. 1: Structure of nicotinamide (nia) free ligand

Measurements

The elemental analyses of carbon, hydrogen and nitrogen contents were performed using a Perkin Elmer CHN 2400 (USA). The molar conductivities of freshly prepared 1.0×10^{-3} mol/cm³ dimethylsulfoxide (DMSO) solutions were measured for the dissolved nia complexes using Jenway 4010 conductivity meter. The electronic absorption spectra of nia complexes were recorded in DMSO solvent within 900-200 nm range using a UV2 Unicam UV/Vis Spectrophotometer fitted with a quartz cell of 1.0 cm path length. The infrared spectra with KBr discs were recorded on a Bruker FT-IR Spectrophotometer (4000-400 cm⁻¹). The ¹H NMR spectra were recorded on Varian Mercury VX-300 NMR spectrometer. ¹H spectra were run at 300 MHz spectra in deuterated dimethylsulphoxide (DMSO-d₆). Chemical shifts are quoted in δ and were related to that of the solvents. The thermal studies TG/DTG-50H were carried out on a Shimadzu thermogravimetric analyzer till 800°C. Scanning electron microscopy (SEM) images were taken in Quanta FEG 250 equipment. The X-ray diffraction patterns for the selected nia complexes were recorded on X 'Pert PRO PANanalytical X-ray powder diffraction, target copper with secondary monochromate.

Antibacterial and antifungal activities

Antimicrobial activity of the tested samples was determined using a modified Kirby-Bauer disc diffusion method¹⁸. Briefly, 100 μ L of the best bacteria/fungi were grown in

10 mL of fresh media until they reached a count of approximately 10⁸ cells/mL for bacteria or 10⁵ cells/mL for fungi¹⁹. 100 µL of microbial suspension was spread onto agar plates corresponding to the broth in which they were maintained. Isolated colonies of each organism that might be playing a pathogenic role should be selected from primary agar plates and tested for susceptibility by disc diffusion method^{20,21}. Of the many media available, National Committee for Clinical Laboratory Standards (NCCLS) recommends Mueller-Hinton agar due to: it results in good batch-to-batch reproducibility. Disc diffusion method for filamentous fungi tested by using approved standard method (M38-A) developed by the NCCLS²² for evaluating the susceptibility of filamentous fungi to antifungal agents. Disc diffusion method for yeast developed standard method (M44-P) by the NCCLS²³. Plates inoculated with filamentous fungi as *Aspergillus Flavus* at 25°C for 48 hours; Gram (+) bacteria as *Staphylococcus Aureus*, *Bacillus subtilis*; Gram (-) bacteria as *Escherichia Coli*, *Pseudomonas aeruginosa* they were incubated at 35-37°C for 24-48 hours and yeast as *Candida Albicans* incubated at 30°C for 24-48 hours and, then the diameters of the inhabitation zones were measured in millimeters¹⁸. Standard discs of Tetracycline (antibacterial agent), Amphotericin B (antifungal agent) served as positive controls for antimicrobial activity but filter disc impregnated with 10 µL of solvent (distilled water, chloroform, DMSO) were used as a negative control.

The agar used is Mueller-Hinton agar that is rigorously tested for composition and pH. Further the depth of the agar in the plate is a factor to be considered in the disc diffusion method. This method is well documented and standard zones of inhabitation have been determined for susceptible values. Blank paper disks (Schleicher & Schuell, Spain) with a diameter of 8.0 mm were impregnated 10 µL of tested concentration of the stock solutions. When a filter paper disc impregnated with a tested chemical is placed on agar the chemical will diffuse from the disc into the agar. This diffusion will place the chemical in the agar only around the disc. The solubility of the chemical and its molecular size will determine the size of the area of chemical infiltration around the disc. If an organism is placed on the agar it will not grow in the area around the disc if it is susceptible to the chemical. This area of no growth around the disc is known as a "Zone of inhibition" or "Clear zone". For the disc diffusion, the zone diameters were measured with slipping calipers of the National for Clinical Laboratory Standers²⁰. Agar-based methods such as Etest disk diffusion can be good alternatives because they are simpler and faster than broth methods^{24,25}.

RESULTS AND DISCUSSION

The physical and elemental analysis data and compositions of the nia complexes are given in Table 1. The experimental of elemental analyses data indicated that Mg(II), Ca(II),

Sr(II), Ba(II) complexes contain one mole of nicotinamide moiety unit. Based on the stoichiometry between metal ions and nia ligand, the physical and analytical data (Table 1) for the synthesized nicotinamide complexes is in good agreement with the proposed molecular formulas viz. $[\text{Mg}(\text{nia})(\text{Cl})_2(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$ (**1**), $[\text{Sr}(\text{nia})(\text{Cl})_2(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ (**2**), $[\text{Ba}(\text{nia})(\text{Cl})_2(\text{H}_2\text{O})_3] \cdot 9\text{H}_2\text{O}$ (**3**), and $[\text{Ca}(\text{nia})(\text{Cl})_2(\text{H}_2\text{O})_3]$ (**4**) (Where nia=nicotinamide ligand).

Table 1: Analytical and physical data for nicotinamide metal complexes

Complexes empirical formula (M.wt.)	Color	Λ_m (Ω^{-1} $\text{cm}^{-1}\text{mol}^{-1}$)	Elemental analysis (%) found (Calcd.)			
			C	H	N	M
$[\text{Mg}(\text{nia})(\text{Cl})_2(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$ (325.43)	White	30	21.93 (22.14)	5.48 (5.58)	8.55 (8.61)	7.13 (7.47)
$[\text{Sr}(\text{nia})(\text{Cl})_2(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ (352.71)	White	21	21.25 (20.43)	4.53 (4.00)	8.25 (7.94)	24.53 (24.84)
$[\text{Ba}(\text{nia})(\text{Cl})_2(\text{H}_2\text{O})_3] \cdot 9\text{H}_2\text{O}$ (546.54)	White	34	12.68 (13.19)	5.17 (5.53)	4.84 (5.13)	24.97 (25.13)
$[\text{Ca}(\text{nia})(\text{Cl})_2(\text{H}_2\text{O})_3]$ (287.18)	White	27	25.69 (25.10)	4.61 (4.21)	9.98 (9.76)	13.65 (13.96)

Molar conductance

The molar conductance values for the Mg(II), Ca(II), Sr(II), Ba(II) nicotinamide complexes (1.0×10^{-3} mol/cm³) were determined in DMSO. These values were found between 21 and 34 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ indicating a non-electrolytic nature^{26,27}. The observed decrease in electrolytic nature of these complexes is due to the presence of chloride ions inside the coordination sphere. The presence of chloride ions were detected by the addition of silver nitrate reagent leading to the formation of white precipitate.

Infrared spectra

The infrared spectra of nicotinamide complexes (Fig. 2) contain the characteristic absorption bands of nia (Table 2). The strong-to-broad bands existed in the region *ca.* 3400-3300 cm^{-1} were assigned to the $\nu(\text{O-H})$ vibrations of the water molecules in **1**, **2**, **3**, and **4** complexes.

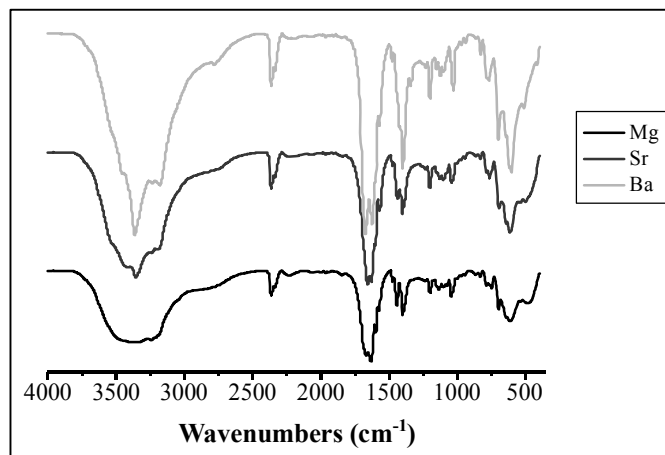


Fig. 2: Infrared spectra of Mg(II), Sr(II) and Ba(II) nia complexes

Infrared data led to the following points which are very important to draw fundamental information about the structural aspects of complexes:

(1) The stretching asymmetric and symmetric vibration spectra of ν (N-H) amide group in free nia appeared at 3375 and 3175 cm^{-1} , respectively, this bands shifted to higher values in Ca(II), Ba(II) and Sr(II) complexes because of hydrogen bonds. In Mg(II) complexes the ν_{as} (N-H) shifted to lower value with disappearance of ν_{s} (N-H), this indicative of contribution of NH_2 group in the bonding by formation of hydrogen bonds with water molecules, which located in the metal coordination field. This supported by appears of boat band at 2750 cm^{-1} , which indicate there is more than one hydrogen bond, whereas Ca(II), Sr(II), and Ba(II) complexes records one value at 2785, 2744, 2783 cm^{-1} , respectively.

(2) The ν (CO) band of solid primary amides is expected to be higher than 1699 cm^{-1} .¹⁹ This band appears in studied complexes spectra as a strong bands at 1672, 1669, 1656, 1680 for Mg(II), Ca(II), Sr(II), Ba(II) complexes, respectively (Table 2) with blue shift, similar observation were reported in literature¹¹ and this behavior was suggested to be a result of combined factors such as the degree of conjugation of carbonyl group with the pyridine ring and the influence of intermolecular hydrogen bond interaction^{15,28}.

(3) δ (NH_2) in Ca(II), Sr(II), Ba(II) complexes have the same value in free ligand, which confirms that the NH_2 group didn't involved in coordination but it participated in hydrogen bonds. On the other hand, the value of δ (NH_2) in Mg(II) complexes is higher than its counterparts in other complexes, this means increasing of the number of hydrogen bonds between NH_2 group and water molecules in Mg(II) complexes.

(4) The new two intensity bands in the region of 600 – 400 cm^{-1} are assigned to M-O and M-N vibrations²⁹.

(5) All complexes have coordinated or uncoordinated water molecules which appear in the infrared spectral data as a broad band overlapped with the stretching vibration bands of NH_2 of amide group.

(6) Pyridine ring vibration of free nia at 1598, 1580 and 1484 cm^{-1} were distorted and had shifted to lower values in spectra of metal complex indicate that pyridine nitrogen is coordinated³⁰.

Table 2: IR spectral data of nia free ligand and nia complexes

Compounds	Assignments					
	NH_2		Hydrogen bonding	$\nu(\text{CO}) + \nu(\text{CN})$	$\delta(\text{NH}_2)$	$\nu(\text{M-N}) + \nu(\text{M-O})$
	$\nu_{\text{as}}(\text{NH}_2)$	$\nu_{\text{s}}(\text{NH}_2)$				
Nia	3375	3175	2787	1699, 1680	1620	--
$[\text{Mg}(\text{nia})(\text{Cl})_2(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$	3357	--	2785	1669	1633	611, 494
$[\text{Sr}(\text{nia})(\text{Cl})_2(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$	3422	3183	2744	1656	1628	617, 541, 505, 430
$[\text{Ba}(\text{nia})(\text{Cl})_2(\text{H}_2\text{O})_3] \cdot 9\text{H}_2\text{O}$	3460	3164	2783	1680	1619	621, 603, 513, 410
$[\text{Ca}(\text{nia})(\text{Cl})_2(\text{H}_2\text{O})_3]$	3446	3179	2785	1672	1616	641, 526

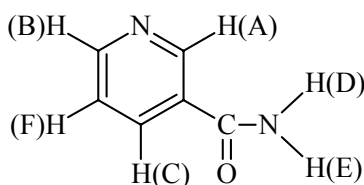
Electronic spectra

Electronic spectra assignment is important to provide fundamental information about the structural aspects of complexes. Nicotinamide ligand has absorption bands in the region of 200 to 400 nm and in some cases this bands extends over higher wavelength region due to conjugation¹⁷. As expected the complexations cause an interesting change in the electronic properties of the system. UV-visible peaks corresponding to $\pi-\pi^*$ transition extended from 270-290 nm with red shift¹⁷. The peaks belonging to $n-\pi^*$ transition of NH_2 and carbonyl of amide group beside to nitrogen atom of pyridine ring recorded a wavelength extended from 362-406 nm^{31-38} . All bands have red shift after complexation.

Proton nuclear magnetic resonance

^1H NMR spectra of nicotinamide free ligand and both Mg(II) and Ba(II) complexes were recorded in DMSO- d_6 taking TMS as internal standards. Nicotinamide free ligand (Scheme 1) has assigned as: δ (ppm) 9.081 (1H(A), pyridine ring), 8.735 (1H(B), pyridine ring), 8.249 (1H(C), pyridine ring), 7.527 (1H(F), pyridine ring), 8.220 and 7.670 (2H(D&E), NH_2 of amide group).

Mg(II) complex: δ (ppm) = 9.059, 9.051 (H(A), pyridine ring), 8.667-8.646 (1H(B), pyridine ring), 8.509 (1H(C), pyridine ring) 8.322-8.283 (1H(D), NH_2 of amide group. 7.617 (1H(E), 7.487-7.443 (H(F), pyridine ring) signal at 3.878 assignment for water molecules. Ba(II) complex: δ (ppm) 9.041-9.033 (H(A), pyridine ring), 8.698-8.677 (1H(B), pyridine ring), 8.266-8.214 (1H(C), pyridine ring) + (1H(D), NH_2 of amide group. 7.615 (1H(E), 7.510-7.464 (H(F) pyridine ring) signal at 3.388 due to water molecules. The proton NMR spectra of all complexes show the ligand resonance down field shifted as compared to that of the free ligand because of adjacent of nicotinamide molecules linked by hydrogen bonds.



Position of protons	δ - Chemical shift (ppm)
A	9.081
B	8.735
C	8.249
D	8.220
E	7.670
F	7.527

Scheme 1: Proton positions and δ -chemical shift (ppm) of free nicotinamide ligand

Scanning electron microscopy and X-ray powder diffraction

The microstructure, surface morphology and chemical composition of barium (II) nicotinamide complex were studied using scanning electron microscopy. Typical scanning electron micrograph is shown in Fig. 3.

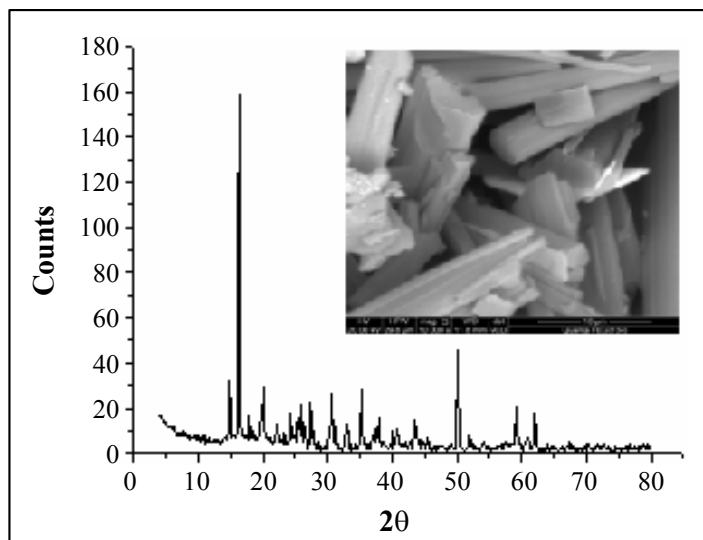


Fig. 3: XRD spectra fitted with SEM photo of $[\text{Ba}(\text{nia})(\text{Cl})_2(\text{H}_2\text{O})_3] \cdot 9\text{H}_2\text{O}$ complex

The surface morphology of SEM micrograph reveals the well sintered nature of the Ba (II) complex with uniform grain sizes and shapes. The distribution of the grain size is homogeneous and has stick shapes. The average particle size of the Ba(II) complex was found to be 2.5 μm . The X-ray powder diffraction patterns in the range of $4^\circ < 2\theta < 80^\circ$ was carried in order to obtain an idea about the lattice dynamics of the barium (II) complex. X-ray diffraction of this complex was recorded compatible with SEM and shown in Fig. 3. The values of 2θ , d value (the volume average of the crystal dimension normal to diffracting plane), full width at half maximum (FWHM) of prominent intensity peak, relative intensity (%) and particle size of barium (II) complex was calculated. The maximum diffraction patterns of $[\text{Ba}(\text{nia})(\text{Cl})_2(\text{H}_2\text{O})_3] \cdot 9\text{H}_2\text{O}$ complex exhibited at $2\theta = 16^\circ$. The crystallite size could be estimated from XRD patterns by applying FWHM of the characteristic peaks using Deby-Scherrer Equation 1.³⁹

$$D = K\lambda / \beta \cos\theta \quad \dots(1)$$

Where D is the particle size of the crystal gain, K is a constant (0.94 for Cu grid), λ is the x-ray wavelength (1.5406 \AA), θ is the Bragg diffraction angle and β is the integral peak width. The particle size was estimated according to the highest value of intensity compared with the other peaks. These data gave an impression that the particle size located within nano scale range.

Suggested structures

The nicotinamide synthesized complexes were characterized using elemental analyses and spectroscopic methods. On the basis of spectral data, 1 : 1 stoichiometry were found for the metal:nia ligand. Non-electrolytic nature of the studied complexes showing the anions is coordinated to the central metal ion. Based on the spectral data the proposed geometries of the studied complexes are depicted in Fig. 4.

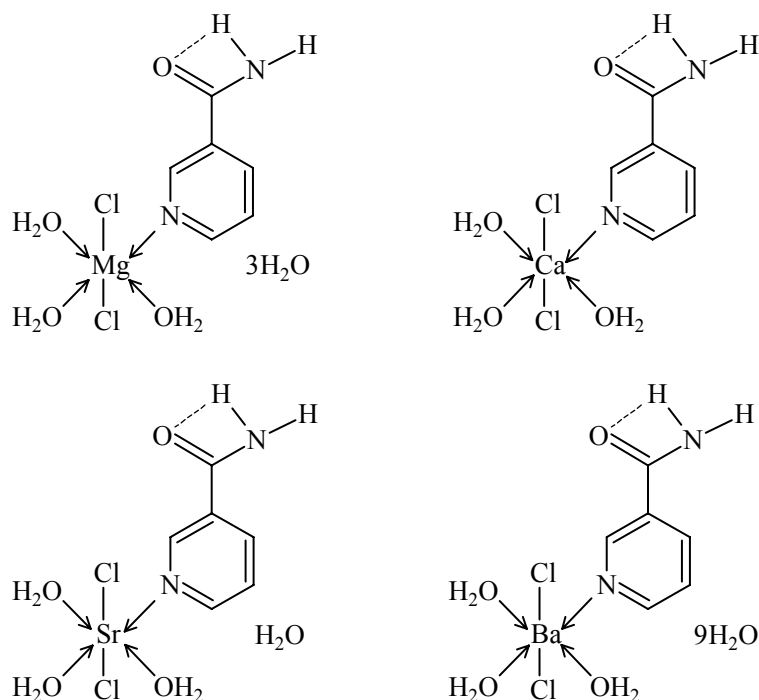
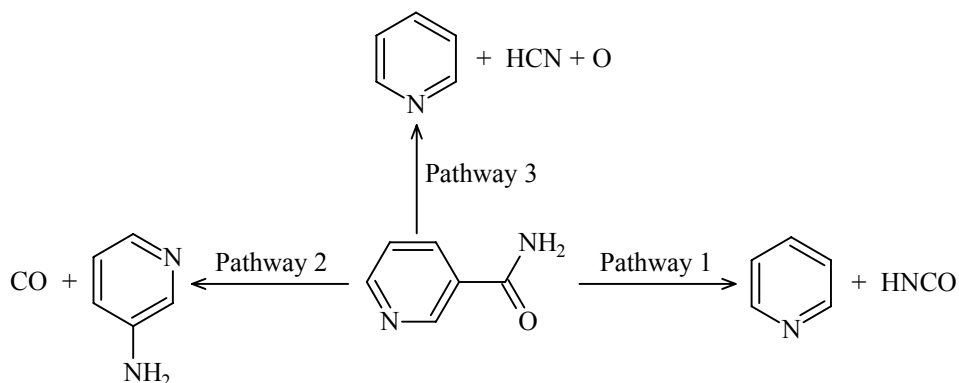


Fig. 4: Suggested structures of Mg(II), Sr(II) and Ba(II) nia complexes

Thermal studies

The TG curves corresponding to decomposition of $[\text{Mg}(\text{nia})(\text{Cl})_2(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$ (**1**), $[\text{Sr}(\text{nia})(\text{Cl})_2(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ (**2**), $[\text{Ba}(\text{nia})(\text{Cl})_2(\text{H}_2\text{O})_3] \cdot 9\text{H}_2\text{O}$ (**3**), and $[\text{Ca}(\text{nia})(\text{Cl})_2(\text{H}_2\text{O})_3]$ (**4**) complexes are displayed in Fig. 5. These plots suggest that decomposition occurs in at least two major detectable steps. Generally, the first step corresponds to an endothermic volatilization of uncoordinated or coordinated of water molecules. The second or third step does not referred to a single process but rather is reflective of two or three overlapping processes and attributed to the nicotinamide ligand alone or accompanied by chlorine groups according to the metal salt used. The degradation of nicotinamide coordinated ligand moving through three pathways as follows;



Proposed degradation mode of nicotinamide ligand

The thermal decomposition data of all nicotinamide complexes are summarized in above Scheme. Thermogravimetric analysis (TGA) representative curves corresponding to the Mg(II), Ca(II), Sr(II) and Ba(II) nia complexes are presented in Fig. 5. The thermal fragmentation Scheme for the nia complexes is shown below; the thermal decomposition occurs in two-to-three steps. The endothermic decomposition steps inserted between 30–455°C, 30–604°C, 30–325°C and 30–800°C for the Mg(II), Ca(II), Sr(II) and Ba(II) nia complexes, respectively, with mass loss 98%, 80%, 58% and 64%, which attributed to decomposition process of coordinated and uncoordinated water molecules, chloride ions, and nia molecule. The residual mass observed are 12.38%, 19.53%, 41.86% and 36.11% which is nearly equal to experimental values, due to the formation of stable compounds like MgO, CaCO₃, SrCO₃ and BaCO₃, respectively.

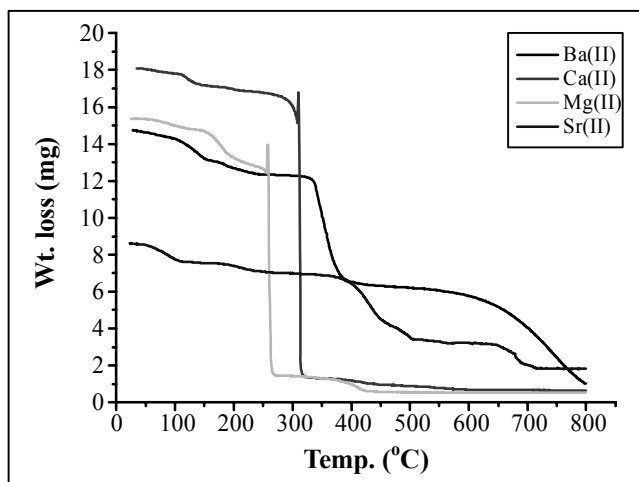


Fig. 5: TG diagrams of Mg(II), Ca(II), Sr(II) and Ba(II) nia complexes

Antimicrobial studies

The antibacterial and antifungal activities data of the nia metal complexes were introduced as inhibition zone diameter (mm/mg sample) Fig. 6, all nia complexes have not recorded any significant inhibition against four different bacteria, against gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*) and gram-negative (*Escherichia coli* and *Pseudomonas aeruginosa*) and two strains of fungus (*Aspergillus flavus* and *Candida albicans*), except for $[\text{Ca}(\text{nia})(\text{Cl})_2(\text{H}_2\text{O})_3]$ complex which has a mild antibacterial efficiency towards *Pseudomonas aeruginosa*. The activity increases with increase in concentration of the test solution containing respected complexes, thus chelation increases lipophilic character in the complexes and results in enhancement of activity⁴⁰.

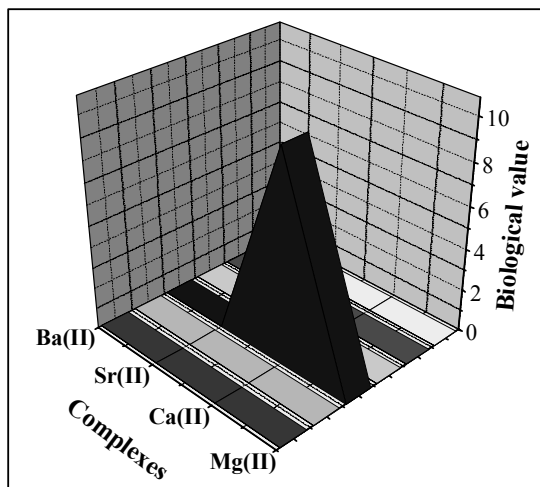


Fig. 6: Antimicrobial tests of Mg(II), Ca(II), Sr(II) and Ba(II) nia complexes

ACKNOWLEDGEMENT

This work was supported by grants from Princess Nora Bint Abdul Rahman University, Riyadh, Saudi Arabia under Project Grants No. 22/32.

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Revised : 16.05.2013

Accepted : 19.05.2013