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Synthesis, spectroscopic characterization, thermal analysis and electrical conductivity studies of Mg(II), Ca(II), Sr(II) and Ba(II) vitamin B2 complexes

Moamen S. Refat [a,b,*], Mohamed A.A. Moussa [c,d], Soha F. Mohamed [e]

[a] Department of Chemistry, Faculty of Science, Port Said University, Port Said, Egypt
[b] Department of Chemistry, Faculty of Science, Taif University, 888 Taif, Saudi Arabia
[c] Department of Physics, Faculty of Science, Taif University, 888 Taif, Saudi Arabia
[d] Department of Physics, Faculty of Science, Mansoura University, Mansoura 35516, Egypt
[e] Department of Chemistry, Faculty of Science, Zagazig University, Egypt

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ABSTRACT

Riboflavin (RF) complexes of Mg(II), Ca(II), Sr(II) and Ba(II) were successfully synthesized. Structures of metal complexes obtained were confirmed and characterized by elemental analysis, molar conductance, and infrared spectra. DC electrical conductivity measurements indicated that the alkaline earth metal (II) complexes of RF ligand are non-electrolytes. Elemental analysis of chelates suggest that the metal(II) ligand ratio is 1:2 with structure formula as $[M(RF)_2(X)_2]\cdot nH_2O$. Infrared assignments clearly show that RF ligand coordinated as a bidentate feature through azomethine nitrogen of pyrazine ring and C=O of pyrimidine-2,4-dione. Thermal analyses of Mg(II), Ca(II), Sr(II) and Ba(II) complexes were investigated using (TG/DSC) under atmospheric nitrogen between 30 and 800 °C. The surface morphology of the complexes was studied by SEM. The electrical conductivities of RF and its metal complexes were also measured with DC electrical conductivity in the temperature range from room to 483 K.

1. Introduction

The application of inorganic compounds to medicine requires detailed examination of the fundamental aqueous chemistry of the proposed drug, including its pharmacokinetics, the metabolic fate in blood and intracellularly, and the effects of the drug on the target of choice. Coordination and organometallic complexes present a wide variety of coordination spheres, ligand designs, oxidation states, and redox potentials, giving the ability to systematically alter the kinetic and thermodynamic properties of the complexes toward biological receptors [1]. The medicinal uses and applications of metals and metal complexes are of increasing clinical and commercial importance [2–8]. The field of inorganic chemistry in medicine may usefully be divided into two main categories: firstly, ligands as drugs which target metal ions in some form, whether free or protein-bound; and secondly, metal-based drugs and imaging agents where the central metal ion is usually the key feature of the mechanism of action [9].

Riboflavin (Fig. 1) is a member of the B family of vitamins (B complex). Riboflavin is a water-soluble vitamin and excess amounts are excreted through the kidneys. It makes the urine fluorescent yellow. Riboflavin is an important antioxidant. Like the other B vitamins, riboflavin plays an important role in energy production. Riboflavin is one of the series of enzymes called flavoproteins. There are over 40 known flavoproteins, all playing important roles in the oxidation processes in the body that help create energy. Because riboflavin is fluorescent under UV light, dilute solutions (0.015–0.025% w/w) are often used to detect leaks or to demonstrate coverage in an industrial system such a chemical blend tank or bioreactor [10–12]. There is little attention in the literature about the complexation of RF [13,14]. Riboflavin is converted to its radical cation and dihydro derivatives RFH_2 using In(I), V(II), Eu(II) and Ti(III) [13]. The analogous conversions of RF into radical cation and RFH_2 were also established by the treatment of RF in 1.0 M $HClO_4$ using calculated amount of Eu(II) and V(II) via consecutive single electron transactions [15].

For the first time Malele et al. [14] synthesized and characterization RF–Mo(V) complex in powder form by elemental analysis, UV–Vis, IR, ^1H NMR spectroscopy and X-ray diffraction study along with the steady state spectroscopic studies of the $[Mo_2O_4(H_2O)_6]^{2+}$ complex being used as a precursor for the synthesis of the RF complex. Our research group has been trended in a synthesized, structural, spectroscopic characterization, thermal behavior and kinetic investigation of the thermal decomposition processes occurring through the metal ions drug interactions [16–24]. As a continuation in this trend, the main task of this paper is synthesized and characterizing the structures of the 1:2 metal:ligand Mg(II), Ca(II), Sr(II) and Ba(II) complexes with riboflavin and to interpretative in details its

* Corresponding author at: Department of Chemistry, Faculty of Science, Taif University, 888 Taif, Saudi Arabia.
E-mail address: msrefat@yahoo.com (M.S. Refat).

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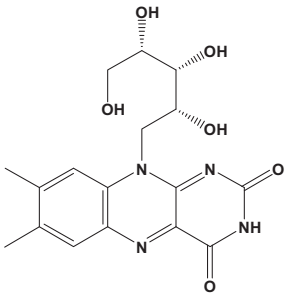

Fig. 1. Riboflavin (RF) structure.

thermal behavior using TGA and DSC but complementary techniques: scanning electron microscopy (SEM), FT-IR spectroscopy. A possible decomposition pathway is also proposed for all the decomposition steps according to the weight losses recorded by the TG probe. In addition, DC electrical conductivity measurements, as a function of temperature, were also carried out to have an idea about the type of conduction mechanism in these compounds.

DC electrical conductivity: Intensive research activities on organic semiconducting materials have led to insights into their chemical and physical properties. In the present investigation DC electrical measurements were carried out on $MgCl_2$, $CaCl_2$, $SrCl_2$ and $Ba(NO_3)_2$ RF complexes as a function of temperature. These measurements gave an idea about electronic structure and identification of the conduction mechanisms operating in different samples. Thermally generated hole concentration, hole mobility, total trap concentration and depth of the trap level are estimated. In organic compound samples that are not macroscopic single crystals conduction can be dominated by variable-range-hopping (VRH) [25]. We have applied the VRH model to this sample in the low temperature region, and hopping conduction parameters are determined for different samples.

2. Experimental

Riboflavin, $MgCl_2$, $CaCl_2$, $SrCl_2$ and $Ba(NO_3)_2$ were purchased from Fluka and used without further purification. Reagents and solvents were purchased from commercial sources and were of analytical grade.

2.1. Synthesis of $MgCl_2$, $CaCl_2$, $SrCl_2$ and $Ba(NO_3)_2$ RF complexes

A solutions of $MgCl_2$, $CaCl_2$, $SrCl_2$ and $Ba(NO_3)_2$ with 0.095 g, 0.111 g, 0.159 g and 0.208 g (1 mmol), respectively, in bi-distilled water (5 mL) was added dropwise to a stirred suspended solution of RF (0.753 g, 2 mmol) in ethanol (20 mL). The resulting yellow–orange solution was refluxed with stirring for 5 h at 75 °C. The solid orange yellow precipitated was filtered off, washed with ethanol and dried under vacuum.

2.2. Physical and tool of analysis

Elemental analysis CHN contents were determined using CHNS-932 (LECO) Vario Elemental analyzers. The percentage of Mg(II), Ca(II), Sr(II) and Ba(II) metals in RF complexes form was determined gravimetrically by the direct ignition of the RF complexes at 1000 °C in static air for 3 h till constant weight. The residue was then weighted in the forms of metal oxide. To confirm the presence or absence of chloride content in the RF complex, the AgCl solution as a precipitating agent was used as described elsewhere [26]. The mid infrared spectra of the resulted RF complexes were measured from KBr disks using a Shimadzu FT-IR spectrophotometer with number of scan 10 and resolution equal 4 cm^{-1}. Molar conductance measurements in DMSO solvent at 25 °C for the reactants and their Mg(II), Ca(II), Sr(II) and Ba(II)/RF complexes with concentration 1.0×10^{-3} mol/L were carried out using Jenway 4010 conductivity meter. DSC thermograms of the RF complexes were obtained on a SCINCO DSC 1500 STA. Sample in solid form were placed in aluminum pans with a pierced lid, and heated rate of 10 °C min^{-1} under a nitrogen flow. TGA was carried out on a SCINCO TGA 1500 STA apparatus at a heating rate of 10 °C min^{-1}under nitrogen atmosphere. Scanning electron microscopy (SEM) images were taken in JEOL-840 equipment, with an accelerating voltage of 15 kV.

2.3. Theoretical calculation

The rate-dependent parameters of solid state non-isothermal decomposition reactions can be determined by analysis of TG curves. The rate of a decomposition process can be described as the product of two separate functions of temperature and conversion using

$$d\alpha/dt = k(T)f(\alpha) \quad (1)$$

where α, is the fraction decomposed at time t, $k(T)$ is the temperature dependent function and $f(\alpha)$ is the conversion function dependent on the mechanism of decomposition. It has been established that the temperature dependent function $k(T)$ is of the Arrhenius type and can be considered as the rate constant k.

$$k = Ae^{-E^*/RT} \quad (2)$$

where R and A, are the gas constant in (kJ deg^{-1} mol^{-1}) and frequency factor (s^{-1}), respectively. Substituting Eq. (2) into Eq. (1), we get,

$$d\alpha/dT = (A/\varphi e^{-E^*/RT})f(\alpha) \quad (3)$$

where φ, is the linear heating rate dT/dt. On integration and approximation, this equation can be obtained in the following form

$$\ln g(\alpha) = -E^*/RT + ln[AR/\varphi E^*] \quad (4)$$

where $g(\alpha)$, is a function of α dependent on the mechanism of the reaction. The integral on the right-hand side is known as

Table 1
Physical, analytical, and molar conductance data of the Mg(II), Ca(II), Sr(II) and Ba(II) RF complexes.

Compounds	Found (calc.)				Molar conductance
	%C	%H	%N	%M	Ω^{-1} cm^2 mol^{-1}
RF	54.20	5.31	14.88	–	12
$[Mg(RF)_2(Cl)_2]$	(−48.11)	(−4.72)	(−13.21)	(−2.87)	21
	47.88	4.65	13.11	2.75	
$[Ca(RF)_2(Cl)_2]$	(−47.23)	(−4.63)	(−12.96)	(−4.64)	20
	47.12	4.55	12.85	4.49	
$[Sr(RF)_2(Cl)_2]$	(−44.77)	(−4.39)	(−12.29)	(−9.61)	18
	44.62	4.24	11.95	9.49	
$[Ba(RF)_2(NO_3)_2]$	(−40.23)	(−3.94)	(−11.04)	(−13.54)	24
	40.04	3.88	10.89	13.25	