

# Synthesis and spectrothermal studies of vitamin B13 complexes of cobalt(II) and nickel(II) with 4-methylimidazole: Crystal structure of $[\text{Ni}(\text{HOr})(\text{H}_2\text{O})(4\text{-Meim})_3]_2 \cdot 5\text{H}_2\text{O}$

Okan Zafer Yeşilel<sup>a,\*</sup>, Mustafa Serkan Soylu<sup>b</sup>, Halis Ölmez<sup>c</sup>, Orhan Büyükgüngör<sup>d</sup>

<sup>a</sup> Department of Chemistry, Faculty of Arts and Sciences, Eskişehir Osmangazi University, 26480 Eskişehir, Turkey

<sup>b</sup> Department of Physics, Giresun Faculty of Arts and Sciences, Karadeniz Technical University, Giresun, Turkey

<sup>c</sup> Department of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Kurupelit, Samsun, Turkey

<sup>d</sup> Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Kurupelit, Samsun, Turkey

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## Abstract

The aquatris(4-methylimidazole)orotatocobalt(II),  $[\text{Co}(\text{HOr})(\text{H}_2\text{O})(4\text{-Meim})_3]$  (**1**) and bis[aquatris(4-methylimidazole)orotatonicel(II)] pentahydrate,  $[\text{Ni}(\text{HOr})(\text{H}_2\text{O})(4\text{-Meim})_3]_2 \cdot 5\text{H}_2\text{O}$  (**2**) have been synthesized and characterized by means of elemental analysis, thermal analysis, IR, UV–Vis and mass spectroscopic studies. The crystal structure of **2** was also determined by single crystal X-ray diffraction. The Ni(II) complex contains the isomers  $\Lambda$  and  $\Delta$  of  $[\text{Ni}(\text{HOr})(\text{H}_2\text{O})(4\text{-Meim})_3]$ , self-assembled through complementary  $\pi$ – $\pi$  and C–H  $\cdots$   $\pi$  interactions, leading to an intricate two-dimensional array. The Co(II) and Ni(II) ions in  $[\text{M}(\text{C}_5\text{H}_2\text{N}_2\text{O}_4)(\text{H}_2\text{O})(\text{C}_4\text{H}_6\text{N}_2)_3]$  are chelated to the deprotonated N3 pyrimidine atom and to the carboxylate oxygen atom of the bidentate orotate dianion, and to the three nitrogen atoms of the 4-Meim ligands, and their octahedral geometries are completed by an aqua ligand. The thermal decomposition pathway of the complexes has been predicted by the help of thermal analysis (TG, DTG and DTA) and mass spectroscopic data. © 2006 Elsevier Ltd. All rights reserved.

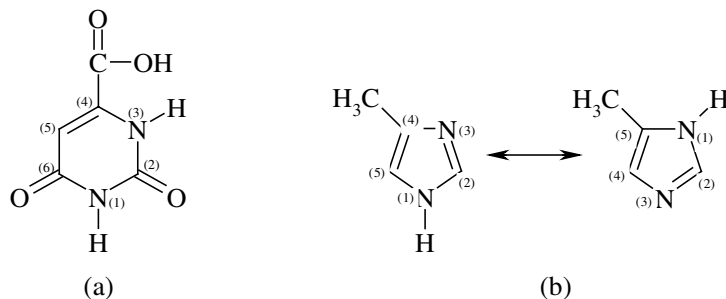
**Keywords:** Orotate complexes; 4-Methylimidazole; Thermal decomposition

## 1. Introduction

Vitamin B13 (Orotic acid,  $\text{H}_3\text{Or}$ , Scheme 1(a)) and its derivatives are of great importance in biological systems, due to their significance in biosynthesis of pyrimidine nucleotides of DNA [1–3]. In recent years, research in bio-inorganics has revealed the important role of metal ions in most biological processes. For these reasons, metal orotates have recently attracted growing attention in medicine. Furthermore, nickel, magnesium, palladium and platinum orotate complexes have been screened as therapeutic agents for cancer [4]. Recent interest has focused on the proposed biological carrier function of orotic acid and the corre-

sponding anionic species for metal ions, which is held responsible for the obviously successful application of metal orotates in curing syndromes associated with a deficiency of a variety of metals such as calcium, magnesium, zinc or iron [5,6]. The orotato anion may exhibit versatile coordinating modes such as monodentate [7–12], bidentate [13–30], bridging ligand [30–35] and counter anion [36–39]. In this study, we describe the preparation, spectroscopic characterization (IR and UV–Vis) of orotate complexes of Co(II) (**1**) and Ni(II) (**2**) with 4-methylimidazole (Scheme 1(b)). The 4-methylimidazole coordinated to the metal ions appears to be 5-methylimidazole due to the steric effect of methyl groups. The first thermal decomposition pathway of the complexes has been predicted with the help of thermal analysis (TG, DTG and DTA) and mass spectroscopic data. The crystal structure of **2** has also been determined by single crystal X-ray diffraction.

\* Corresponding author. Tel.: +90 02222393750.  
E-mail address: [yesilel@ogu.edu.tr](mailto:yesilel@ogu.edu.tr) (O.Z. Yeşilel).



Scheme 1. Structures of the ligands: (a) vitamin B13; (b) 4(5)-methylimidazole tautomers.

## 2. Experimental

### 2.1. Preparation of the complexes

A solution of 4-Meim (0.82 g, 10 mmol) in methanol (10 ml) was added dropwise with stirring to a solution of  $[\text{Co}(\text{HOr})(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$  [24] (0.76 g, 2.5 mmol) or  $[\text{Ni}(\text{HOr})(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$  [20] (0.76 g, 2.5 mmol) in distilled water (30 ml). The solution was heated to 60 °C in a temperature-controlled bath and then stirred for 5 h at 60 °C. The reaction mixture was then cooled to room temperature. The red and blue crystals formed for the Co(II) and Ni(II) complexes, respectively, were filtered and washed with 10 ml of cold distilled water and methanol, and dried in air. *Anal. Calc.* for  $\text{C}_{17}\text{H}_{22}\text{N}_8\text{O}_5\text{Co}$ : C, 42.78; H, 4.65; N, 23.47. *Found*: C, 43.02; H, 4.52; N, 23.24%. *Anal. Calc.* for  $\text{C}_{34}\text{H}_{54}\text{N}_{16}\text{O}_{15}\text{Ni}_2$ : C, 39.11; H, 5.21; N, 21.46. *Found*: C, 39.12; H, 5.28; N, 21.74%.

### 2.2. Materials and measurements

All chemicals used were analytical reagent products. The elemental and mass spectroscopic analysis was carried out in TÜBİTAK Marmara Research Centre of Turkey. Mass spectroscopic analysis was performed on a Fisons MD 800 mass spectrometer coupled to a Fisons 8000 GC and FAB ionisation source. Magnetic susceptibility measurements at room temperature were performed using a Sherwood Scientific MXI model Gouy magnetic balance. The UV–Vis spectra were obtained for an aqueous solution of the complexes ( $10^{-3}$  M) with a Unicam UV2 spectrometer in the range 900–190 nm. The IR spectra were recorded in the 4000–400  $\text{cm}^{-1}$  region with a Mattson 1000 FT-IR spectrometer using KBr pellets. A TG8110 thermal analyzer was used to record simultaneous TG, DTG and DTA curves in static air atmosphere at a heating rate of 10  $\text{K min}^{-1}$  in the temperature range 20–1000 °C using platinum crucibles. Highly sintered  $\alpha\text{-Al}_2\text{O}_3$  was used as a reference and the DTG sensitivity was 0.05  $\text{mg s}^{-1}$ .

### 2.3. Crystallographic analysis

Data collection was performed on a STOE IPDS II image plate detector using Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Intensity data were collected in the  $\theta$

range 1.87–28.08° at 100 K. Data collections: Stoe X-Area [40]. Cell refinement: Stoe X-Area [40]. Data reduction: Stoe X-RED [40]. The structure was solved by direct-methods using SIR97 [41] and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on  $F^2$  using SHELXL-97 [42]. Molecular drawings were obtained using ORTEP-III [43] and DIAMOND [44]. All H atoms except for water hydrogens were treated as riding. Restrain was applied to water hydrogens to idealized geometry.

## 3. Results and discussion

### 3.1. UV–Vis spectra and magnetic susceptibility

The  $\lambda_{\text{max}}$  values of the two absorption bands in the UV–Vis spectra of **1** are 384 ( $\epsilon = 22 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) and 522 nm ( $\epsilon = 34 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). These values were assigned to the following d–d transitions,  $\nu_3$ :  ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$  and  $\nu_2$ :  ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$ , respectively.  $\nu_1$ :  ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$  transition was not observed which is of low energy and shifts to the IR region and the  $\Delta_0$  values for **1** could not be calculated. The electronic spectrum of **2** in  $\text{H}_2\text{O}$  exhibits two absorption bands at 540 and 884 nm and the corresponding  $\epsilon$  values are 21 and 18  $\text{L mol}^{-1} \text{ cm}^{-1}$ , respectively. These values were assigned to  $\nu_2$ :  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$  and  $\nu_1$ :  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$  d–d transitions. The  $\Delta_0$  value for **2** was calculated as 11300  $\text{cm}^{-1}$  since  $\Delta_0 = \nu_1$  for  $d^8$  complexes [45].

The complexes **1** and **2** exhibit magnetic moment values of 4.27 and 2.41 BM which corresponds to three and two unpaired electrons, respectively, which are consistent with

Table 1  
IR spectra of the complexes<sup>a</sup> ( $\text{cm}^{-1}$ )

Complexes	<b>1</b>	<b>2</b>
$\nu\text{OH}$	3544 s	3498 m
$\nu\text{N}_{(3)}\text{H}$ ; $\nu\text{NH}_{\text{Meim}}^*$	3255 m*	3222 m*
$\nu\text{N}_{(1)}\text{H}$	3207 m	3176 m
$\nu\text{CH}$	3087–2971 w	3012–2873 w
$\nu\text{C}=\text{O}_{\text{acid}} + \nu\text{C}_{(2)}=\text{O}$	1639 s	1614 vs, b
$\nu\text{C}_{(6)}=\text{O} + \nu\text{C}=\text{C}$	1620 s	
$\nu\text{C}=\text{N}_{\text{HOr}}$ ; $\nu\text{C}=\text{N}_{\text{Meim}}^*$	1483 m	1487 m
$\delta\text{N}_{(1)}\text{H}$ ; $\delta\text{NH}_{\text{Meim}}^*$	1427 w; 1373 m*	1398 m; 1371 m*
M–O; M–N	522 w; 466 w	576 w; 444 w

<sup>a</sup> Abbreviations: w – weak; m – medium; s – strong; vs – very strong, b – broad.

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