

# Synthesis, properties and crystal structure of a Zn,Nb compound with homo- and heterodinuclear oxalate-bridged units – $[\{Zn(bpy)_2\}_2(\mu-C_2O_4)][Zn(bpy)_2(\mu-C_2O_4)NbO(C_2O_4)_2]_2 \cdot 0.5bpy \cdot 7H_2O$ : The impact of weak interactions on the crystal packing

Marijana Jurić<sup>a</sup>, Pavica Planinić<sup>a,\*</sup>, Nevenka Brničević<sup>a</sup>, Dubravka Matković-Čalogović<sup>b</sup>

<sup>a</sup> Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia

<sup>b</sup> Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10000 Zagreb, Croatia

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## Abstract

A heterometallic Zn,Nb compound of the formula  $[\{Zn(bpy)_2\}_2(\mu-C_2O_4)][Zn(bpy)_2(\mu-C_2O_4)NbO(C_2O_4)_2]_2 \cdot 0.5bpy \cdot 7H_2O$  (1) (bpy = 2,2'-bipyridine) has been synthesized by the reaction of the tris(oxalato)oxoniobate(V) anion,  $[NbO(C_2O_4)_3]^{3-}$  and  $[Zn(bpy)_3]^{2+}$  in an aqueous solution, and characterized by IR and UV/vis spectroscopy, elemental and thermogravimetric analyses and X-ray single crystal diffraction method. The compound crystallizes in the triclinic  $P\bar{1}$  space group with  $a = 15.9060(9)$ ,  $b = 16.0804(9)$ ,  $c = 21.5892(12)$  Å,  $\alpha = 69.504(4)$ ,  $\beta = 82.598(5)$ ,  $\gamma = 86.012(5)^\circ$ ,  $V = 5127.5(5)$  Å<sup>3</sup>, and  $Z = 2$ . The molecular structure consists of three dinuclear oxalate-bridged units, one homodinuclear  $Zn^{II}Zn^{II}$  and two heterodinuclear  $Zn^{II}Nb^V$  units, seven water molecules and half of a bipyridine molecule. Zinc atoms are in all units octahedrally surrounded by four nitrogen atoms from the bipyridine ligands and by two oxygen atoms from the bridging oxalate groups. Niobium atoms in the two mixed  $Zn^{II}Nb^V$  units adopt a pentagonal bipyramidal coordination formed by six oxygen atoms from the oxalate groups and one oxo-oxygen atom. Weak interactions, primarily hydrogen bondings and  $\pi$ - $\pi$  stacking interactions, influence greatly the supramolecular motifs recognized in the crystal packing. Thermal decomposition of the title compound resulted in the formation of the mixed-metal  $Zn_3Nb_2O_8$  oxide phase.

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**Keywords:** Zinc–niobium compound; Oxalate bridges; Homodinuclear ZnZn units; Heterodinuclear ZnNb units; Hydrogen bonding network;  $Zn_3Nb_2O_8$  phase

## 1. Introduction

There has been a constant growing interest in the last decade or so for novel solid-state architectures with potential applications as functional materials in the fields such as catalysis, conductivity, luminescence or magnetism [1–6]. In the rational approaches to the design and synthesis of various metal-organic coordination polymers with specific chemical and physical properties, a key role belongs to

the nature of the metal ion and the geometry, flexibility and coordination preferences of the bridging ligands.

The reach binding facilities of the oxalate  $C_2O_4^{2-}$  anion, and its ability of mediating magnetic exchange interaction between the paramagnetic metal centres are responsible for the existence of a huge number of oxalate-bridged transition metal species, of different nuclearity and dimensionality [7–9]. The use of stable mononuclear anionic oxalate complexes,  $[M^{III}(C_2O_4)_3]^{3-}$  ( $M^{III} = Cr, Mn, Fe, Ru$ ) as ligands toward another metal ion provides a very efficient way for the synthesis of heterometallic oxalate-bridged 2D and 3D assemblies, which also exert a range of distinct magnetic properties [10].

\* Corresponding author. Tel.: +385 1 4561 189.

E-mail address: [planinic@irb.hr](mailto:planinic@irb.hr) (P. Planinić).

Zinc(II)  $\mu$ -oxalate complexes, as magnetically uninteresting species, have been studied to a somewhat lesser extent than those of copper(II) or other transition metals. However, polynuclear zinc(II) and other  $d^{10}$  metals complexes, in general, have been paid extensive attentions for their appealing optic properties and structural topology. Zinc(II) is a particularly attractive metal cation for chemosensing because unlike other metal cations, it does not quench the fluorescence of an attached dye and it is not redox active. A respective number of reports deal with this property as a promising characteristic for the use in different optical devices [11,12].

There is a particularly great importance of zinc complexes in the field of synthetic and biological chemistry, due to the role this element plays in biological systems – fulfilling structural and different catalytic functions in a great number of enzymes [13]. Apart from enzymes with one zinc-binding site, enzymes with two or three zinc ions connected by bridging ligands are of particular interest, with the most distinguished feature that their activity is a function of the Zn···Zn separation. On that account, dinuclear homo- and heterometallic zinc(II) complexes are often used as model compounds in order to simulate the characteristic properties of the active sites in metalloenzymes [14].

Our continuous research interest is related to the design and synthesis of transition metal polynuclear complex compounds, with the aim of obtaining potentially new functional materials. Recently, we have reported a number of oxalate-bridged transition metal complexes, synthesized by the use of mononuclear anionic tris(oxalate) ligands, like  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$  and  $[\text{NbO}(\text{C}_2\text{O}_4)_3]^{3-}$ , and various transition metal cations as building blocks, and exerting ferromagnetic exchange interactions within homodinuclear ( $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$ ) as well as heterotrimeric ( $\text{Cu}^{\text{II}}\text{Cr}^{\text{III}}\text{Cu}^{\text{II}}$ ) units [15,16]. By extending our investigation to zinc(II), in the reaction of tris(oxalato)oxoniobate(V) anion,  $[\text{NbO}(\text{C}_2\text{O}_4)_3]^{3-}$  and  $[\text{Zn}(\text{bpy})_3]^{2+}$ , a compound of interesting architecture, containing simultaneously two types of dinuclear oxalate-bridged units ( $\text{Zn}^{\text{II}}\text{Zn}^{\text{II}}$  and  $\text{Zn}^{\text{II}}\text{Nb}^{\text{V}}$ ) and analysed as  $[\{\text{Zn}(\text{bpy})_2\}_2(\mu\text{-C}_2\text{O}_4)]\{\text{Zn}(\text{bpy})_2(\mu\text{-C}_2\text{O}_4)\text{NbO}(\text{C}_2\text{O}_4)_2\}_2 \cdot 0.5\text{bpy} \cdot 7\text{H}_2\text{O}$  (**1**) (bpy = 2,2'-bipyridine) has been obtained. Although heterometallic zinc(II) complexes are numerous [17,18], dinuclear units containing  $\text{Zn}^{\text{II}}$  and  $\text{Nb}^{\text{V}}$  are not known.

Polymeric chain structures dominate within the structurally characterized oxalate-bridged zinc(II) complexes with N-donor ligands, with  $\text{C}_2\text{O}_4^{2-}$  acting in a bis(didentate) bridging mode, as found for the compounds  $[\text{Zn}(\text{C}_2\text{O}_4)\text{L}]_n$  (L = 2,2'-bipyridine) [19a],  $\{[\text{Zn}(\text{C}_2\text{O}_4)\text{L}] \cdot 2\text{H}_2\text{O}\}_n$  (L = ethylenediamine) [19b],  $\{[\text{Zn}(\text{C}_2\text{O}_4)\text{L}_2] \cdot \text{H}_2\text{O}\}_n$  or  $[\text{Zn}(\text{C}_2\text{O}_4)\text{L}_2]_n$  (L = pyridine) [19c,19d]. With L = 4,4'-bipyridine, two-dimensional polymers have been obtained, like those in  $[\text{Zn}(\text{C}_2\text{O}_4)\text{L}]_n$  [20a] and  $[\text{Zn}_3(\text{C}_2\text{O}_4)_3\text{L}_4]_n$  [20b,20c]. The use of 1,2-bis(4-pyridyl)ethane (bpa) and 1,2-bis(4-pyridyl)ethylene (bpe) allowed the synthesis of the  $[\text{Zn}(\text{C}_2\text{O}_4)(\text{bpa})]_n$  and  $[\text{Zn}(\text{C}_2\text{O}_4)(\text{bpe})]_n$  compounds with a 2D rectan-

gular grid-type network, wherein infinite  $[\text{Zn}(\text{C}_2\text{O}_4)]_n$  chains are cross-linked by the organic spacers [20d]. The reaction of  $\text{Zn}^{2+}$  ions with organoammonium oxalates has been shown to yield zinc oxalates of various dimensionalities [19d,21]. In the zero-dimensional  $[\text{C}_4\text{N}_2\text{H}_{12}]_3[\text{Zn}_2(\text{C}_2\text{O}_4)_5] \cdot 4\text{H}_2\text{O}$  compound the dimeric zinc oxalate is strongly hydrogen bonded to the diprotonated piperazine and water molecules [21a], and the one-dimensional zinc oxalate chain in the  $\{[\text{C}_6\text{N}_2\text{H}_{14}][\text{Zn}(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}\}_n$  compound, where  $\text{C}_6\text{N}_2\text{H}_{12} = 1,4\text{-diazabicyclo}[2.2.2]\text{octane}$ , is also stabilized by extensive hydrogen bonding [21a]. The 2D layered oxalates, like  $\{[\text{C}_6\text{H}_8\text{N}]_2[\text{Zn}_2(\text{C}_2\text{O}_4)_3]\}_n$  ( $\text{C}_6\text{H}_8\text{N} = \text{methylpyridinium cation}$ ) [19d],  $\{\text{K}[\text{C}_6\text{N}_2\text{H}_{13}][\text{Zn}_2(\text{C}_2\text{O}_4)_3] \cdot 4\text{H}_2\text{O}\}_n$  ( $\text{C}_6\text{N}_2\text{H}_{13} = \text{monoprotonated } 1,4\text{-diazabicyclo}[2.2.2]\text{octane}$ ) [21b],  $\{[(\text{CH}_3)_2\text{NH}(\text{CH}_2)_3\text{NH}_3][\text{Zn}_2(\text{C}_2\text{O}_4)_3] \cdot 2\text{H}_2\text{O}\}_n$  [21c] or  $\{[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3][\text{Zn}_2(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}\}_n$  [21d] adopt the common honeycomb structures with 12-membered apertures – six Zn and six oxalate groups. The 3D zinc oxalate from this series, of the empirical formula  $\{2[\text{C}_3\text{H}_7\text{NH}_3][\text{Zn}_2(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}\}_n$  possesses honeycomb layers cross-linked by oxalate units [21d].

A detailed structural analysis of **1** proved the significance of the hydrogen bonds and  $\pi$ – $\pi$  stacking interactions in proliferating one-dimensional structures into two- and three-dimensional crystalline framework. Herein we report the synthesis, spectroscopic and thermogravimetric analyses and the crystal structure of the new compound.

## 2. Experimental

### 2.1. Materials and measurements

All reagents used in the synthesis were purchased from commercial sources and used without further purification.  $\text{Na}_3[\text{NbO}(\text{C}_2\text{O}_4)_3] \cdot 4\text{H}_2\text{O}$  and  $[\text{Zn}(\text{bpy})_3]\text{Cl}_2 \cdot 7\text{H}_2\text{O}$  were prepared according to the literature methods [22,23]. Infrared spectra were recorded as KBr pellets on an ABB Bomem FT model MB 102 spectrometer, in the 4000–200  $\text{cm}^{-1}$  region. Electronic spectra were measured with a Cary 50 Probe spectrophotometer. The samples were prepared as KBr pellets which were mounted in the pathway of the radiation beam, and a weighed pure-KBr pellet was used as the reference. Thermogravimetric measurements were carried out on a Shimadzu DTG-60H analyser, with a heating rate of 10  $^\circ\text{C min}^{-1}$  in the stream of synthetic air. X-ray powder diffraction patterns of the samples thermally treated on the thermobalance were recorded on an Oxford Xcalibur Nova R diffractometer with a micro-focus tube using  $\text{CuK}\alpha$  radiation. The samples were placed in a 0.3 mm diameter capillary.

### 2.2. Synthesis of $[\{\text{Zn}(\text{bpy})_2\}_2(\mu\text{-C}_2\text{O}_4)]\{\text{Zn}(\text{bpy})_2(\mu\text{-C}_2\text{O}_4)\text{NbO}(\text{C}_2\text{O}_4)_2\}_2 \cdot 0.5\text{bpy} \cdot 7\text{H}_2\text{O}$ (**1**)

After mixing an aqueous solution (10 mL) of  $\text{Na}_3[\text{NbO}(\text{C}_2\text{O}_4)_3] \cdot 4\text{H}_2\text{O}$  (0.2024 g; 0.3938 mmol) with an aqueous solution (5 mL) of  $[\text{Zn}(\text{bpy})_3]\text{Cl}_2 \cdot 7\text{H}_2\text{O}$  (0.1439 g; 0.1969 mmol)

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