

# Synthesis, structure and properties of Ni(II) coordination polymer based on $\alpha,\alpha$ -dimethyl substituted zoledronate



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We dedicate this paper to Professor Tadeusz Lis on the occasion of his 70th birthday.

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## ABSTRACT

The reaction of  $\alpha,\alpha$ -dimethyl substituted derivative of zoledronic acid with Ni(II) afforded 1D coordination polymer,  $\text{Ni}_3(\text{HL})_2(\text{H}_2\text{O})_6 \cdot 6\text{H}_2\text{O}$  (**1**). The title compound possess crystallographically and spectroscopically distinct Ni1 and Ni2 centers characterized by tetragonality distortion parameter  $T = 0.97$  and 1.04, respectively, and is isomorphous with recently reported  $\text{Co}_3(\text{HL})_2(\text{H}_2\text{O})_6 \cdot 6\text{H}_2\text{O}$  complexes based on  $\alpha,\alpha$ -dimethyl and cyclopropyl substituted zoledronate derivatives.

Detailed analysis of thermal stability of **1** revealed that partly dehydrated  $[\text{Ni}_3(\text{HL})_2(\text{H}_2\text{O})_3]$  still retains its architecture and structural integrity of coordinated ligands. Exploring supramolecular interactions that build up the crystal of **1** and related Co(II) complexes allowed a conclusion that distinct dehydration pathways observed for each compound may be correlated with subtle differences in 3D crystals packing.  $\text{Ni}_2(\text{P}_2\text{O}_7)$  salt was identified as the major final product of thermolysis of **1**.

The magnetic properties of **1** analyzed in term of a spin-1 Heisenberg  $\text{Ni}_2\text{Ni}_1\text{Ni}_2$  trimer chains model revealed antiferromagnetic  $\text{Ni}_1 \cdots \text{Ni}_2$  interactions within the trimers ( $J_1 = -7.32 \text{ cm}^{-1}$ ) and ferromagnetic  $\text{Ni}_2 \cdots \text{Ni}_2$  intertrimers coupling ( $\Theta_W = 1.72 \text{ K}$ ). Furthermore, different values of the axial zfs  $D$  parameters and the  $g$ -factors were assigned to the Ni1 and Ni2 centers.

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## 1. Introduction

In recent years a steady growth of importance of metal organophosphonates has been observed. This class of compounds is an object of interest not only due to their ability to create coordination compounds of varying complexities with different metal ions [1] but also because of their potential applications in gas storage and sorption [2], catalysis [3] or as luminescent [4], magnetic [5] or biomedical materials [6,7]. A feature that allows organophosphonic acids to form various types of metal complexes is the presence of tetrahedral phosphonic/phosphonate groups with multiple O-donor atoms able to coordinate and bridge multiple metal ions. Furthermore, phosphonic and/or phosphonate groups can act as proton donors and acceptors, hence build coordination networks which dimensionalities are predominantly dictated by their protonation state. A specific architecture of final product can additionally be determined by several factors such as e.g. structural requirements of ligand, a charge and geometrical preferences of

the central atom, temperature or metal-to-ligand stoichiometric ratio.

A widely studied group of organophosphonate compounds are bisphosphonic acids, especially in the field of medical science [8]. The pharmaceutical importance of bisphosphonic acids is dictated by their ability to inhibit the bone resorption process, which is crucial for the treatment of skeletal disorders such as osteoporosis [9] or Paget's disease [10]. The most effective antiresorptive agent [11] and currently the one of the most studied ligands in the field of supramolecular chemistry is zoledronic acid – 1-hydroxy-2-(1H-imidazol-1-yl)ethylidenebisphosphonic acid ( $\text{H}_4\text{Zol}$ ). Among coordination compounds based on zoledronate ligand reported so far have been examples of 0D isolated coordination units [12], 1D linear coordination polymers [13], 2D layers [14] or 3D coordination networks [15].

Recently, we developed new zoledronic acid derivatives functionalized at  $C_\alpha$  carbon by methyl groups or cyclopropane ring [16] and used them to construct two isomorphous 1D coordination polymers of general formula  $\text{Co}_3(\text{HL})_2(\text{H}_2\text{O})_6 \cdot 6\text{H}_2\text{O}$ . Both compounds comprise alternately arranged  $[\text{Co}_2(\text{HL})(\text{H}_2\text{O})_2]_2$  and  $[\text{Co}_1\text{O}_6]$  coordination units, in which crystallographically distinct

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Co2 and Co1 centers display slightly compressed and slightly elongated six-coordinated environment, respectively. An analysis of magnetic behavior of both compounds in term of a spin-3/2 Heisenberg Co2Co1Co2 trimer chains revealed that Co1···Co2 interactions within the trimer are antiferromagnetic whereas Co2···Co2 intertrimer interactions are ferromagnetic [17].

In continuation of our research on the design and investigation of metal complexes based on  $\alpha,\alpha$ -disubstituted derivatives of zole-dronic acid we used thus obtained 1-hydroxy-2-(1H-imidazol-1-yl)-2-methylpropylidene-1,1-diphosphonic acid ( $H_4L$ , Scheme 1) [16] to synthesize  $Ni_3(HL)_2(H_2O)_6 \cdot 6H_2O$  complex **1**, shown by single-crystal X-ray diffraction to be isomorphous with previously reported Co(II) complexes. Herein, we report its crystal structure, spectroscopic characterization by means of IR and NIR-UV/VIS techniques and detailed investigations on thermal stability and magnetic properties. Interestingly, cyclopropyl derivative of zole-dronic acid [17] did not yield a crystalline product with Ni(II) under similar conditions.

Several Ni(II) complexes based on parent zole-dronate ligand have also been prepared and characterized structurally. Cao et al. published structures of  $Ni(H_3Zol)_2(H_2O)_4$  and  $Ni_3(HZol)_2(H_2O)_4 \cdot 2H_2O$  with two different architectures – 0D discrete coordination unit and 2D coordination layer [18]. Additionally, 3D coordination networks comprising  $[Ni_3(HZol)_2]$  coordination units and 4,4'-bipyridine or 4,4'-vinylenedipyridine acting as auxiliary ligands have been reported [19,20]. All the complexes mentioned above have been an object of interest mainly due to their magnetic properties.

## 2. Experimental

### 2.1. Materials

All reagents and solvents were used as received without further purification. 1-Hydroxy-2-(1H-imidazol-1-yl)-2-methylpropylidene-1,1-diphosphonic acid ( $H_4L$ ) was synthesized according to previously described procedure [16]. Details of synthesis and purification of  $H_4L$  are reported in Ref. [17].

### 2.2. Synthesis of $Ni_3(HL)_2(H_2O)_6 \cdot 6H_2O$ (**1**)

$H_4L$  (0.10 mmol, 0.0300 g) was dissolved in water (5 ml). Then, 0.15 mmol (0.0395 g) of  $NiSO_4 \cdot 6H_2O$  was added. The pH of resulting clear solution was adjusted to 4.4 with 1 M NaOH. The reaction mixture was sealed in a glass tube and heated at 100 °C for 72 h. After the reaction system had been cooled slowly to room temperature, greenish, block crystals of **1** were isolated, washed with distilled water and dried at room temperature. Crystals were collected as a monophasic material based on the powder XRD (Fig. S1, ESI). Yield 29.2 mg (59.2% based on  $H_4L$ ). Elemental Anal. found (calc.) for  $C_{14}H_{46}Ni_3N_4O_{26}P_4$  (%): C, 16.84 (17.04); H, 4.59 (4.71); N, 5.52 (5.68). IR (ATR,  $cm^{-1}$ ): 3153br & w, 3048w, 2948w, 1637w, 1575w, 1531w, 1477w, 1458w, 1388w, 1359w, 1313w, 1249w, 1199w, 1177w, 1124m, 1083s, 1050m, 1031m, 995s, 954m,

935m, 890m, 852m, 752m, 736m, 689s, 650s, 623s, 575s, 544s, 519s, 497s, 466s, 411s.

### 2.3. X-ray crystallography

Crystallographic measurement was performed on an Agilent Technologies Xcalibur R automated four-circle diffractometer with graphite monochromatized Mo  $K\alpha$  radiation at 100(2) K, using an Oxford Cryosystems cooler. Data collection, cell refinement, data reduction and analysis were carried out with CrysAlisPro [21]. Empirical (multi-scan) absorption correction was applied to the data with use of CrysAlisPro. The refinement of the described structure was started by using the coordinates of heavy (non-H) atoms taken from previously reported  $Co_3(HL)_2(H_2O)_6 \cdot 6H_2O$  complex based on the same ligand [17] and further refined on  $F^2$  by a full-matrix least squares technique with SHELXL-2014 [22] with anisotropic thermal parameters for all the non-H atoms (except for lower-occupied position of the disordered O6W water molecule, which was refined with the O atom in two sites, with SOFs of 0.848 (12):0.152(12), and H atoms modeled as common for the two positions of the O atom). H atoms were found in difference Fourier maps and were refined isotropically. In the final refinement cycles, all C- and most of the O-bound H atoms (excluding water H atoms) were repositioned in their calculated positions and refined using a rigid model, with C–H = 0.95–0.98 Å and with  $U_{iso}(H) = 1.5U_{eq}(CH_3)$  and  $1.2U_{eq}(CH)$ . N- and O-bound H atoms were refined with the N–H and O–H bond lengths restrained to 0.880(2) and 0.840(2) Å, respectively, and with  $U_{iso}(H) = 1.2U_{eq}(N)$  or  $1.5U_{eq}(O)$ , and then constrained to ride on their parent atoms (AFIX 3 instruction in SHELXL). Additionally, the H···H distances in the water molecules were restrained to 1.380(2) Å. All figures were made using DIAMOND program [23].

**Crystallographic data:** CCDC No. 1562494,  $C_{14}H_{46}N_4Ni_3O_{26}P_4$ ,  $M_r = 986.56$ , greenish block, crystal size  $0.20 \times 0.06 \times 0.05$  mm, triclinic space group  $P\bar{1}$  (No. 2),  $a = 9.462(2)$ ,  $b = 9.767(3)$ ,  $c = 10.301(3)$  Å,  $\alpha = 82.92(2)$ ,  $\beta = 73.92(2)$ ,  $\gamma = 64.89(2)^\circ$ ,  $V = 828.3(4)$  Å<sup>3</sup>,  $T = 100(2)$  K,  $Z = 1$ ,  $\rho_{calc} = 1.978$  g cm<sup>-3</sup>,  $\mu = 1.99$  mm<sup>-1</sup> (for Mo  $K\alpha$ ,  $\lambda = 0.71073$  Å),  $T_{min} = 0.920$ ,  $T_{max} = 1.000$ , 6548 reflections measured, 3781 unique ( $R_{int} = 0.033$ ), 2954 observed [ $I > 2\sigma(I)$ ],  $(\sin \theta/\lambda)_{max} = 0.681$  Å<sup>-1</sup>, 239 parameters, 22 restraints,  $R[F^2 > 2\sigma(F^2)] = 0.042$ ,  $wR(F^2) = 0.085$ ,  $S = 1.06$ , largest difference in peak and hole  $\Delta\rho_{max}$ ,  $\Delta\rho_{min} = 0.59, -0.48$  e Å<sup>-3</sup>, respectively.

### 2.4. Powder X-ray diffraction analysis

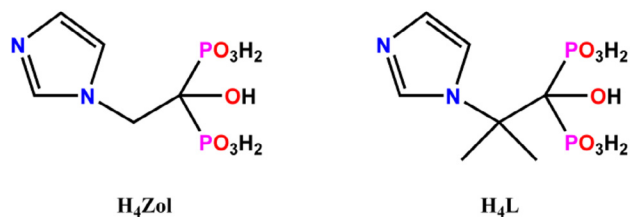
PXRD data were collected on a Bruker D8-Advance diffractometer equipped with a VANTEC-1 detector ( $\lambda_{CuK\alpha 1} = 1.5406$  Å). The equipment was operated at 30 kV and 40 mA, and data were collected at room temperature in the range of  $2\theta = 5$ –50°.

### 2.5. ATR FT-IR measurements

The ATR FT-IR (ATR is attenuated total reflectance) spectra were recorded on a Bruker Vertex 70v Fourier transform IR spectrometer equipped with a diamond ATR cell. The spectral data were collected at room temperature over the range 4000–400  $cm^{-1}$  with a resolution of 4  $cm^{-1}$ . Instrument control and initial data processing were performed using OPUS software (v. 7.0 Bruker Optics, Ettlingen, Germany).

### 2.6. Thermal analysis

Thermogravimetric analysis (TG-DTA) was carried out using a Setaram SETSYS 16/18 analyzer, operating under a nitrogen



Scheme 1. Zoledronic acid and its  $\alpha,\alpha$ -dimethyl substituted derivative.

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