Low pH constructed Co(II) and Ni(II) 1D coordination polymers based on Cα-substituted analogues of zoledronic acid: structural characterization, and spectroscopic and magnetic properties†

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Three novel coordination compounds based on α,α-disubstituted analogues of zoledronic acid with a cyclopropane (cpp) or cyclobutane (cbt) ring on the Cα carbon, isomorphous [Co(H2cppZol)(H2O)]·H2O (1a), [Ni(H2cppZol)(H2O)]·H2O (1b) and [Co(H2cbtZol)(H2O)]·H2O (2a), were synthesized under hydrothermal conditions at low pH. Single-crystal X-ray diffraction analysis revealed that all the compounds had a 1D double zig-zag chain architecture with an 8 + 8 ring motif formed by alternately arranged asymmetrical (−O−P−O−)2 bridges linking equivalent octahedral metal centres. Both the ligand coordination mode and chain architecture displayed by 1a, 1b and 2a are unique among 1D [M(H2L)(H2O)]·yH2O coordination polymers based on nitrogen-containing bisphosphonates reported so far. All the compounds exhibit similar decomposition pathways upon heating with thermal stabilities decreasing in the order 1b > 1a > 2a. The IR spectra revealed that lattice water release above 227, 178 and 97 °C, respectively, does not change the chain architecture leaving them intact up to ca. 320, 280 and 240 °C. Magnetic behaviour investigations indicated that 1a, 2a and 1b exhibit weak alternating antiferromagnetic–ferromagnetic exchange interactions propagated between the magnetic centres through double (−O−P−O−)2 bridges. The boundary between antiferromagnetic–ferromagnetic couplings for the Co−O⋯O−Co angle in 1a and 2a was estimated to be ca. 80°. This value is also applicable for recently reported [M3(HL)2(H2O)6]·6H2O (M = Co, Ni) complexes based on α,α-disubstituted analogues of zoledronic acid and can be used to the explain magnetic behaviour of 1b.

1. Introduction

Organophosphonic acids are a class of ligands widely known for their excellent affinity for metal ions. The propensity to coordinate and bridge various metal centres resulting from multiple O-donor atoms occurring in tetrahedral phosphonic/phosphonate group(s) allows them to form coordination compounds with diverse supramolecular architectures and promising applications in the field of catalysis, gas storage, biotechnology, photoluminescence or magnetism. Therefore, metal-organophosphonate solids belong to an important and extensively developed class of functional materials.

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To explore and expand the area of metal-BPs coordination compounds we have focused our research on new derivatives of zoledronic acid, H$_4$Zol (Scheme 1). This compound is a member of N-containing bisphosphonates family (NBPs), currently considered to be the most potent agent in the treatment of bone diseases and successfully exploited as multidentate ligand suitable for a synthesis of various metal complexes. With the aim to determine how structural modifications of H$_4$Zol imply topologies and architectures of coordination compounds formed with d-block metal ions, we synthesized a series of its derivatives with sterically demanding substituents on C$_n$ atom, such as methyl groups (H$_4$dmtZol), a cyclopropane (H$_4$cppZol), cyclobutane (H$_4$cbtZol) or cyclopentane (H$_4$cptZol) ring. All the ligands were structurally characterized and for their ability to interact with Co(u) and Ni(u) under different pH conditions. Our recent studies have demonstrated that at pH ca. 4.0–5.0, both cations form one-dimensional coordination polymers with a general formula M$_3$(HL)$_2$(H$_2$O)$_6$ or M$_2$(HL)$_2$(H$_2$O)$_4$. In this article we show that carrying the reaction at lower pH –5.0, both cations form one-dimensional coordination chain (Fig. S2b, ESI†). The four-membered ring motif generated by coordination with the use of TG-DTA, DSC, FT-IR, NIR-UV/Vis techniques and magnetic susceptibility measurements. Interestingly, both ligands coordination mode and chains architecture of the reported compounds are unique among NBPs-based [M(H$_2$L)(H$_2$O)$_y$]$_z$-yH$_2$O (x = 0–1, y = 0–3) coordination polymers based on various NBPs. (Table S1, ESI†). Among them, d-block metal complexes of the type [M(H$_2$L)]·xH$_2$O (x = 0–3; M = Cd[n], Zn(u), Mn(u), Co(u), Cu(u); H$_2$L$^{2+}$ = 2-(4-pyridinyl)-1-hydroxyl-1,1-ethylidenediphosphonate; or M = Mn(u), Cd(u), H$_2$L$^{2+}$ = risedronate; M = Mn(u), Cu(u), H$_2$L$^{2+}$ = pamidronate; M = Mn(u), H$_2$L$^{2+}$ = alendronate, zoledronate and [M(H$_2$L)(H$_2$O)] (M = Fe(n), Co(n), Mn(n), H$_2$L$^{2+}$ = risedronate) have been found to reveal the ladder chain architecture. Commonly, in this type of structures, phosphonate μ$_x$-O bridges link two equivalent metal centres into a four-membered (MO$_x$)$_2$ dinuclear unit, whereas phosphonate O–P–O bridges connect adjacent dinuclear units to form eight-membered (M–O–P–O) rings resulting in double 1D infinite chain. It is to note, that formation of such 4 + 8 rings motif along the coordination chain is favoured regardless of varying geometries and nature of metal centres as well as subtle differences in ligands coordination modes (Fig. S1a–d, ESI†). The double zig-zag chain architecture is characteristic for Ca(u) complexes. The four-membered ring motif generated by μ$_x$-O bridges between metal centres is propagated along double chains displayed by seven-coordinate [Ca(H$_2$L)(H$_2$O)]$_2$-H$_2$O and [Ca(H$_2$Zol)(H$_2$O)] (Fig. S2a, ESI†). On the other hand, six-coordinate [Ca(H$_2$Ale)]-H$_2$O complex represents the structure, in which a combination of phosphonate O–P–O and μ$_x$-O bridges between metal centres leads to 6 + 6 rings motif propagated along the coordination chain (Fig. S2b, ESI†).

Herein, we report the structures of 1a, 1b and 2a determined by single-crystal X-ray diffraction and their detailed characterization with the use of TG-DTA, DSC, FT-IR, NIR-UV/Vis techniques and magnetic susceptibility measurements. Interestingly, both ligands coordination mode and chains architecture of the reported compounds are unique among NBPs-based [M(H$_2$L)(H$_2$O)$_y$]$_z$-yH$_2$O coordination polymers reported so far.
2. Experimental

2.1 Materials

All commercially available reagents and solvents were used as received without further purification. 1-Hydroxy-2-[1-(1H-imidazol-1-yl)cyclopropyl]ethylidene-1,1-diphosphonic acid (H₄cppZol) and 1-hydroxy-2-[1-(1H-imidazol-1-yl)cyclobutyl] ethylidene-1,1-diphosphonic acid (H₄cbtZol) were synthesized according to previously described procedure. Details of synthesis and purity confirmation of both ligands are reported in ref. 12 and 13.

2.2 Synthesis of Co(H₂cppZol)(H₂O)·H₂O (1a)

H₄cppZol (0.10 mmol, 0.0298 g) and CoCl₂·6H₂O (0.05 mmol, 0.0119 g) were dissolved in water (5 ml). Then, the pH of the reaction mixture was adjusted to 2.9 by 1 M NaOH. The obtained clear and pink solution 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, pink crystals of 1a were isolated, washed with distilled water and dried at room temperature. Crystals were collected as a monophasic material based on the powder XRD (Fig. S5, ESI†). Yield 16.4 mg (41.6% based on H₄cppZol). Elemental anal. found (calc.) for C₇H₁₄NiN₂O₉P₂ (%): C, 21.66 (21.51); H, 3.40 (3.62); N, 7.01 (7.17). IR (ATR, cm⁻¹): 3606 br & w, 3526 br & w, 3436 br & w, 3176 w, 3151 w, 3119 w, 3057 br & w, 3033 br & w, 3001 br & w, 2966 br & w, 1653 w, 1609 w, 1584 w, 1534 w, 1480 w, 1465 w, 1443 w, 1386 w, 1354 w, 1319 w, 1276 w, 1230 w, 1179 m, 1128 w, 1089 s, 1063 s, 1038 s, 1013 s, 986 s, 948 s, 872 s, 837 s, 786 m, 771 m, 741 m, 655 s, 629 m, 604 s, 537 s, 511 s, 467 s, 439 s.

2.3 Synthesis of Ni(H₂cppZol)(H₂O)·H₂O (1b)

H₄cppZol (0.10 mmol, 0.0298 g) and NiCl₂·6H₂O (0.07 mmol, 0.0167 g) were dissolved in water (5 ml). Then, the pH of the reaction mixture was adjusted to 3.5 by 1 M NaOH. The obtained clear and pink solution 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, pink crystals of 1b were isolated, washed with distilled water and dried at room temperature. Crystals were collected as a monophasic material based on the powder XRD (Fig. S5, ESI†). Yield 21.3 mg (52.2% based on H₂cbtZol). Elemental anal. found (calc.) for C₉H₁₄NiN₂O₉P₂ (%): C, 23.74 (23.71); H, 3.61 (3.99); N, 6.80 (6.92). IR (ATR, cm⁻¹): 3600 br & w, 3526 br & w, 3560 br & w, 3176 w, 3151 w, 3119 w, 3057 br & w, 3033 br & w, 3001 br & w, 2966 br & w, 1653 w, 1609 w, 1584 w, 1534 w, 1480 w, 1465 w, 1443 w, 1386 w, 1354 w, 1319 w, 1276 w, 1230 w, 1179 m, 1128 w, 1089 s, 1063 s, 1038 s, 1013 s, 986 s, 948 s, 872 s, 837 s, 786 m, 771 m, 741 m, 655 s, 629 m, 604 s, 537 s, 511 s, 467 s, 439 s.

2.4 Synthesis of Co(H₂cbtZol)(H₂O)·H₂O (2a)

H₂cbtZol (0.10 mmol, 0.0312 g) and CoCl₂·6H₂O (0.10 mmol, 0.0238 g) were dissolved in water (5 ml). Then, the pH of the reaction mixture was adjusted to 3.5 by 1 M NaOH. The obtained clear and pink solution 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, pink crystals of 2a were isolated, washed with distilled water and dried at room temperature. Crystals were collected as a monophasic material based on the powder XRD (Fig. S5, ESI†). Yield 21.3 mg (52.2% based on H₂cbtZol). Elemental anal. found (calc.) for C₉H₁₄CoN₂O₉P₂ (%): C, 21.70 (21.49); H, 3.31 (3.61); N, 7.09 (7.16). IR (ATR, cm⁻¹): 3605 br & w, 3356 br & w, 3145 w, 3043 br & w, 2936 br & w, 1659 w, 1620 w, 1582 w, 1534 w, 1461 w, 1424 w, 1398 w, 1348 w, 1216 w, 1196 w, 1172 w, 1161 w, 1120 w, 1071 s, 1048 s, 1020 s, 1001 s, 977 m, 946 s, 901 s, 888 s, 874 s, 845 s, 804 m, 791 m, 770 m, 700 m, 655 s, 631 m, 614 s, 560 s, 544 s, 528 s, 488 s, 465 s, 449 s, 410 s.

2.5 X-ray crystallography

Crystallographic measurements for 1a, 1b and 2a were performed on k-geometry diffractometer Agilent Technologies Xcalibur R with a Ruby CCD camera and with graphite monochromatized MoKα radiation at 110, 100 and 80 K, respectively, using an Oxford Cryosystems cooler. Data collection, cell refinement, data reduction and analysis as well as analytical absorption correction were carried out with CrysalisPro. The crystal structures of 1b and 2a were solved with direct methods using SHELXS-97 (ref. 26) and refined on F² by a full-matrix least squares technique with SHELXL-2014 (ref. 27) with anisotropic thermal parameters for all the ordered non-H atoms. As complex 1a is isomorphous with 1b, the refinement was started by using the coordinates of heavy (non-H) atoms taken from 1b and further refined as described above.

H atoms in 1a, 1b and 2a were found in difference Fourier maps and were refined isotropically. In the final refinement cycles, all C-bound H atoms, as well as N-bound H atoms in 1a and 1b, were repositioned in their calculated positions and refined using a rigid model, with C–H = 0.95–0.99 Å, N–H = 0.88 Å, and with Uiso(H) = 1.2Ueq(C, N). The H atoms of hydroxyl group in 1a, 1b and 2a, phosphonate group in 2a and all attached to water molecules were refined with the O–H bond lengths restrained to 0.840(2) Å and with Uiso(H) = 1.5Ueq(O).

Then the AFIX 147 and AFIX 3 riding models were used to constrain phosphate H atoms in 1a, 1b and 2a. Additionally, the H–H distances in the water molecules were restrained to 1.360(2) or 1.380(2) Å in 1a, 1b or 2a, respectively. N-bound H atom in 2a was refined with the N–H distance restrained to 0.880(2) Å and with Uiso(H) = 1.2Ueq(N). Then, it was constrained to ride on its parent N atom (AFIX 3 instruction).

Crystallographic data and structure refinement parameters are summarized in Table 1 and the crystallographic information files (CIFs) deposited at the Cambridge Crystallographic Data Centre (CCDC no. 1940766–1940768) and provided as ESI†. All figures were made using the DIAMOND program. 28

2.6 Powder X-ray diffraction analysis

PXRD data were collected on a Bruker D8-Advance diffractometer equipped with a VÁNTEC-1 detector (λCuκα = 1.5418 Å). The
equipment was operated at 30 kV and 40 mA, and data were collected at room temperature in the range of 2θ = 5–50°.

2.7 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 4000–1000 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).

2.8 Thermal analysis
Thermogravimetric analysis (TG-DTA) was carried out using a Setaram SETSYS 16/18 analyzer, operating under a nitrogen atmosphere, with a heating rate of 5 K min⁻¹ in the range 303–1273 K (sample mass of 10.3, 8.6 and 11.0 mg for 1a, 1b and 2a, respectively). Differential Scanning Calorimetry (DSC) measurements were performed on a Setaram DSC 92 instrument. Samples (3.2–7.0 mg) were contained in alumina pans in the presence of air as the furnace atmosphere. Measurements were performed from ambient temperature up to 219, 314, 387, 457 and 600 °C for 1a, 284, 352, 529 and 600 °C for 1b and 175, 329, 525 and 600 °C for 2a with a heating rate of 5 K min⁻¹.

2.9 NIR-UV/Vis-spectroscopic studies
The NIR-UV/Vis diffuse-reflectance electronic spectra of 1a, 1b, 2a and ligands 1 and 2 were measured on a Cary 500 Scan spectrophotometer over the range 5000–50 000 cm⁻¹ with measure step of 10 cm⁻¹ at room temperature. The spectra were recorded with identical parameters as a white reference sample. To obtain the band positions of components of d-d bands in the spectra of cobalt(iii) (1a, 2a) and nickel(ii) (1b) complexes the variable digital method was used with the following parameters: step = 20 cm⁻¹, α = 400 and N = 40 (1a); step = 20 cm⁻¹, α = 400 and N = 30 (2a); and step = 20 cm⁻¹, α = 500, N = 40 (1b).

2.10 Magnetic measurements
Magnetic susceptibility in the temperature range from 1.7 to 300 K in a field of 100 mT (1a and 2a) or 500 mT (1b) and magnetization up to 5 T were measured with a Quantum Design SQUID magnetometer. Diamagnetic corrections (−202 × 10⁻⁶, −212 × 10⁻⁶ and −202 × 10⁻⁶ emu mol⁻¹ for 1a, 2a and 1b, respectively) were calculated using Pascal’s constants. The
exchange Hamiltonian in the form $H = -J S_1 S_2$ was used consistently throughout the paper. All values of magnetization and magnetic susceptibility are reported per mole of metal.

3. Results and discussion

3.1 Syntheses of 1a, 1b and 2a

Compounds 1a, 1b and 2a were synthesized through hydrothermal reaction at 100 °C for 72 h. However, despite their similarity, obtaining pure phase, the best yield and the highest crystals quality required each reaction to proceed under specific conditions.

Compounds 1a and 1b were synthesized with the use of $\text{H}_4\text{cppZol}$ and $\text{CoCl}_2\cdot6\text{H}_2\text{O}$ or $\text{NiCl}_2\cdot6\text{H}_2\text{O}$ salts. The highest yields and qualities of crystalline products were achieved in a narrow pH range 2.4–2.6 for 1a and 2.8–3.0 for 1b. The decrease in pH below the optimum value resulted in reduction of yield without product deterioration. The increase of pH up to ca. 3.5 lead to increase of the reaction yield accompanied by significant deterioration of 1a and 1b while in the pH range 3.5–4.0 minor amount of previously reported $\text{Co}_2(\text{HcppZol})_2(\text{H}_2\text{O})_6\cdot6\text{H}_2\text{O}$ or unrecognized green amorphous solid were observed, respectively. Regardless of the reaction pH, the excess of ligand was desirable. It was found that optimum $\text{H}_4\text{cppZol} : \text{Co}(\text{II})/\text{Ni}(\text{II})$ molar ratios to obtain pure phases of 1a and 2a are 2–1.5 : 1 and 1.5 : 1, respectively. The use of stoichiometric amount of reagents or an excess of ligand resulted in deterioration of crystals quality and reduction of reaction yield even if the most appropriate pH was reached.

The most favoured pH to obtain optimal crystallinity and reaction yield of 2a is ca. 3.0–4.0. Additionally, both stoichiometric amount of reagents or an excess of ligand ($\text{H}_4\text{cbtZol} : \text{Co}(\text{II})$) molar ratios of 1.5–1:1 can be used. At pH below 3.0, the decrease of yield without negative impact on product quality was observed while a mixture of 2a and unidentified, pink, amorphous impurities were obtained above pH 4.0.

The most appropriate for the synthesis of 1a, 1b and 2a are Co(n) and Ni(n) chloride salts. Additionally, 2a can be obtained when cobalt(n) chloride is replaced by sulphate salt. Attempts to prepare 1a, 1b and 2a by using Co(n)/Ni(n) acetates were unsuccessful.

3.2 Crystal structures of 1a, 1b and 2a

The isomorphous compounds 1a, 1b crystallize in triclinic $P\bar{1}$, and 2a in monoclinic $C2/c$ space group as one-dimensional coordination polymers. Table 1 summarizes all crystal data and structure refinement parameters. Selected geometrical parameters and proposed hydrogen bonds are collected in Tables S2–S4 (ESI†).

The asymmetric units of 1a, 1b and 2a consist of one M1 centre (M1 = Co(n) in 1a and 2a or Ni(n) in 1b), one coordinated $\text{H}_2\text{L}^2$ ligand ($\text{H}_2\text{L}^2 = \text{H}_{2}\text{cppZol}^2$ in 1a and 1b or $\text{H}_{2}\text{cbtZol}^2$ in 2a), one coordinated and one lattice water molecule. In all the compounds, the central atom adopts slightly distorted octahedral geometry with equatorial sites occupied by O2, O7 O4$^{\text{iv/iii}}$ and O1W atoms and axial sites filled by O6, and O1$^{\text{iv/iii}}$ atoms (Fig. 1 and S6, ESI†). The average equatorial and axial M1–O distances calculated based on data from Table S3 (ESI†), of 2.118 and 2.059 Å in 1a, 2.097 and 2.048 Å in 1b and 2.152 and 2.054 Å in 2a, result in tetragonality distortion $T$ index defined as $T = R_{\text{int}}/R_{\text{out}}$ ($R_{\text{int}}$ and $R_{\text{out}}$ are the average in-plane and out-of-plane M–O ($M = \text{Co, Ni}$) distances) of 1.03, 1.02 and 1.05, respectively, thus indicating slight compression of octahedrons along the axial O2–M1–O4$^{\text{iv/iii}}$ bond.

In all 1a, 1b and 2a, coordinated ligands contain protonated imidazole N atom, one fully deprotonated and one monoprotonated phosphonate group yielding the overall charge −2. The values of N1–C2–C1–O7 dihedral angles of 165.1(2)$^\circ$, 165.3(4)$^\circ$ and −172.7(2)$^\circ$, respectively, (Table S2, ESI†) clearly demonstrate the same ap conformation of coordinated $\text{H}_4\text{cppZol}^2$/$\text{H}_4\text{cbtZol}^2$ ligands, recently demonstrated to be rare among NBP's and their anions within coordination compounds and salts. In such arrangement, each ligand exhibits a preference for chelating-bridging mode donating five oxygen atoms to coordinate three M1 (M1 = Co(n)/Ni(n)) ions. The phosphate O2, O6 and hydroxyl O7 atoms coordinate one M1 centre in a tridentate fashion whereas phosphonate O1 and O4 are involved in monodentate binding of two symmetry related M1$^{\text{ii/iv}}$ and M1$^{\text{i/iii}}$. The O5 and protonated O3 atoms remain uncoordinated (Fig. S7, ESI†). As a consequence, the pair of M1 and M1$^{\text{i/iii}}$ ions is connected through O4–P2–O6 phosphate bridges from two equivalent ligands to form dinuclear $[\text{M}_1(\text{H}_2\text{L})(\text{H}_2\text{O})]_2$ unit with puckered, eight-membered (M1–O4–O6–O1ii/iv) conformation of coordinated H2–H2O$^{-}$ interaction (Fig. 2b, S9b and S10b, ESI†). The O7–H7–O6$^{\text{iii/ii}}$ intermolecular hydrogen bond provides additional stabilization of coordination chain (Fig. 2a, S9a and S10a, ESI†). The chains are extended into 2D hydrogen bonded layer by means of N2–H2N–O3$^{\text{v/vii}}$ interaction (Fig. 2b, S9b and S10b, ESI†) and further connected into 3D supramolecular network through O1W–H1W–O6$^{\text{iv/iii}}$ and O1W–H2W–O2$^{\text{ii/iii}}$ hydrogen bonds between coordinated water molecule and phosphate oxygen atoms with formation of R2$^{3}(6)$ ring motif. Additional stabilization of the supramolecular architecture in 1a and 1b is provided by O2W–H3W–O6$^{\text{ii/iv}}$ and O2W–H4W–O1$^{\text{i/ii}}$ interactions involving O2W lattice water molecules as hydrogen donors (Fig. 2c, S9c and S10c, ESI†).

Both ligands binding mode and resulting 8 + 8 rings motif propagated along 1D coordination chains are unique among structures of 1D $[\text{M}_1(\text{H}_2\text{L})(\text{H}_2\text{O})]_2\cdot\text{H}_2\text{O}$ ($x = 0–1$, $y = 0–3$) coordination polymers based on NBP ligands reported so far (Table S1, ESI†). Somewhat similar behaviour is only noted for the $[\text{Zn}(\text{H}_2\text{Ris})]$ complex. However, the fulfilment of both metal and ligand requirements to achieve optimal geometry and energetics leads to tetrahedral geometry maintained by Zn(n) and hydroxyl group of H2Ris$^{3}$ remaining uncoordinated (Table S1, ESI†). As a result, eight-membered (Zn–O–P–O), dinuclear units being common with 1a, 1b and 2a are extended through
twelve-membered rings into polymeric ladder-type structure (Fig. S11, ESI†).

3.3 IR characterization of 1a, 1b and 2a

The FT-IR spectra of the compounds 1a, 1b and 2a are presented in Fig. S12–S15 (ESI†). The bands assignment (Table S5, ESI†) is based on detailed analysis of the IR spectra of H₄dmtZol, H₄cppZol, H₄cbtZol, H₄cptZol ligands supported by DFT calculations (ref. 31, Fig. S16, S17 and Table S6, ESI†) and tentative assignments for Co(II)/Ni(II) coordination polymers reported previously.12–14

The spectra of 1a, 1b and 2a exhibit many common features manifested in location and intensity of characteristic bands assigned to ligand skeleton and functional groups. Additionally, the range 3600–3200 cm⁻¹ is dominated by broad features associated with ν(O–H), ν(PO–H) and ν(N–H) stretching vibrations, consistent with presence of extensive hydrogen bonding involving water molecules (coordinated and lattice), phosphonate and imidazole groups (Table S4, ESI†). A week sharp band at ca. 3150 cm⁻¹ is contributed by ν(C–H) vibrations of imidazole ring. The symmetric and asymmetric C–H stretching vibrations of cyclopropane/cyclobutane CH₂ groups give rise to a set of weak bands in the range 3050–2950 cm⁻¹. The band at ca. 1650 cm⁻¹ corresponds to H–O–H bending vibrations of coordinated and lattice water molecules. The stretching vibrations of imidazole C––C, N––C and N–C bonds contribute weak bands observed at ca. 1580 and 1530 cm⁻¹. The region gathering most of the bending vibrations attributed to imidazole, cyclopropane/cyclobutane rings as well as hydroxyl C–O–H is located between ca. 1500 and 1150 cm⁻¹. Herein, noticeable differences in the spectra are associated with specific deformation vibrations of Cₓ substituents.

The phosphonate groups stretching and bending vibrations absorb mainly below 1350 cm⁻¹. Their detailed analysis supported by DFT calculations (see ref. 31 and Table S6, ESI†) have indicated that ν(P–O) vibrations are usually strongly mixed with δ(P–O–H) and stretching/deformation vibrations of imidazole ring and aliphatic substituents, thus making unambiguous interpretation of experimental IR spectra difficult. The bands near 1350 cm⁻¹ are attributed to δ(P–O–H) vibrations. The ν(P–O) modes of P2 pendant O atom give rise to bands at ca. 1120 and 1030 cm⁻¹. The bands at ca. 945 and 840 cm⁻¹ can be
considered as contributed by $\nu$(P–O) vibrations involving Co(II)/Ni(II)-coordinated phosphonate O atoms. The $\nu$(P–OH) vibrations of P1 group contribute bands at lower 790–770 cm$^{-1}$ wavenumbers. The vibrations contributed mostly by stretching of the C–P bond also appear below 800 cm$^{-1}$. The $\delta$(O–P–O) deformation vibrations of phosphonate groups are observed around 500 cm$^{-1}$.

3.4 Thermal stabilities of 1a, 1b and 2a

Thermal decomposition of 1a, 1b and 2a was investigated on crystalline samples by means of TG-DTA and DSC experiments conducted from room temperature up to 1000/600 °C under nitrogen and air atmosphere, respectively. Fig. 3 compiles TG curves in the temperature range 30–600 °C. Full set of experimental data is collected in Fig. S18–S23 (ESI†).

The studied compounds exhibit similar decomposition pathways with thermal stabilities decreasing in the order 1b > 1a > 2a. The first step, taking place in the temperature ranges 236–271 °C (1b), 190–218 °C (1a) and 121–169 °C (2a), corresponds to release of lattice water molecule accompanied by weight loss of 4.62, 4.54, 5.18% (calcd 4.60, 4.61, 4.45%) with dehydration enthalpies ($\Delta H_r$) of 9.98, 9.12, and 30.7 kJ mol$^{-1}$, respectively. The IR spectra of samples heated up to temperatures at which this process is completed clearly indicate that removal of lattice water has no negative impact on polymeric chains architecture (Fig. S24–S26, ESI†). On further heating up to 600 °C, compounds 1a and 2a behave similarly losing a total 24.4 and 27.9% weight in three distinct exothermic stages with maximum rates of reaction ($T_{max}$) of 303, 367, 430 (1a) and 257, 436, 508 °C (2a). For 1b, only two exothermic processes accompanied by a total weight loss of 15.5% with $T_{max}$ of 340 and 470 °C occur. These processes correspond to collapse of coordination chains by breaking M–O bonds, initiated by release of coordinated water molecule, then followed by elimination of C$_a$-substituents and subsequent release of imidazole rings (Fig. S27–S29, ESI†). However, the IR spectrum shows that in 1b the last process is not completed even at 600 °C (Fig. S30, ESI†).

The last stage of thermal decomposition starts above ca. 700 °C and is characterized by intense 31.5% (1a), 37.7% (1b) and 30.3% (2a) weight losses that can be attributed to combustion of organic parts of ligands. The resultant decomposition products constitute 39.5, 41.1 and 36.7% of initial samples masses and contain likely Co$_2$(P$_2$O$_7$)(1a, 2a) or Ni$_2$(P$_2$O$_7$)(1b) (Fig. S31, ESI†). It is to note, that in contrast to previously analysed Co$_3$(HL)$_2$(H$_2$O)$_6$·6H$_2$O$^{12,13}$ and
Co₃(HL)₂(H₂O)₄·2H₂O, the products of 1a and 2a thermolysis are almost free from other residues (caled 37.3, 36.03%). A support for such conclusion is provided by IR spectra revealing the absence of a weak band at ca. 1300 cm⁻¹ (Fig. S32 and S33, ESI†).

3.5 NIR-UV/Vis spectroscopic characterization of 1a, 1b and 2a

In all 1a, 1b and 2a the donor oxygen atoms form the {MO₄O₂²⁺} chromophore (M = Co(II)/Ni(II)) of pseudo-octahedral geometry compressed along the O₄–M–O₂ bond (Fig. 1 and S6, ESI†). It is to note, that the magnitude of compression increases with the increase of C₄ substituent size (a > b, 2019, 31497). The well seen bands found at 14 010 cm⁻¹ of tetragonally distorted Co²⁺ octahedrons in NaCo₂(SeO₃)₂OH and Na₃Co₂(SeO₃)₂OH salts.

In the compressed tetragonal crystal field of D₄ symmetry, degenerate 4T₁(4F, O₈) level splits into 4A₂ + 4E components where the 4A₂ is the ground state. The next quartet 4T₂(4F, O₈) level consists of 4E + 4B₂ states, while the 4A₂g(4F, O₈) state is nondegenerate and transforms as 4B₁. Likewise, the crystal field of D₄ symmetry causes splitting of the last quartet 4T₁g(4F, O₈) level into 4E and 4A₂ states. As the absorption in 13 500–25 000 cm⁻¹ spectral range is composed of multiple unresolved bands (Fig. 4), the spectra were deconvoluted with the use of variable digital filtering method in order to refine band splitting and obtain energies of its components (Fig. S34, ESI†). The obtained pairs of bands with maxima at 6830 cm⁻¹, 8250 cm⁻¹ (1a) and 6950 cm⁻¹, 8050 cm⁻¹ (2a) are generated by spin-allowed quartet–quartet 4A₂ → 4E and 4A₂ → 4B₂ transitions (4E and 4B₂ states from 4T₂(4F) in O₈). However, the energy values 6830 cm⁻¹ (1a) and 6950 cm⁻¹ (2a) obtained for the 4A₂ → 4E transition are quite ambiguous because of presence of strong ligand bands in the region up to 7000 cm⁻¹. The spin and symmetry forbidden transitions become possible by splitting of the 4E(2G, O₈) state into 4A₁ + 4B₁. Under filtration process the pairs of bands at 10 210 cm⁻¹/12 510 cm⁻¹ (1a) and 10 330 cm⁻¹/12 430 cm⁻¹ (2a) clearly appeared and can be assigned to the 4A₂ → 4A₁ and 4A₂ → 4B₁ transitions, respectively. The well seen bands found at 14 010 cm⁻¹ (1a) and 13 890 cm⁻¹ (2a) originate from the spin-allowed quartet–quartet 4A₂ → 4B₁ transition and are less intense as compared to other spin-allowed transitions. This assignment is drawn based on Wildner research explaining appearance of bands at 13 350 cm⁻¹ and 15 200 cm⁻¹ in the polarized (β polarization) electronic spectra of tetragonally distorted Co²⁺ octahedrons in NaCo₂(SeO₃)₂OH and kieserite-type CoSO₄·H₂O and CoSeO₄·H₂O salts.

The same approach has also been applied to explain the origin of similar bands in the electronic spectrum of [Co₂(HcptZol)₂(H₂O)₄]·2H₂O.
the spectrum of 1a, one band arises at 16 930 cm\(^{-1}\), while for 2a analogous band is splitting into two components with positions at 16 330 cm\(^{-1}\) and 17 170 cm\(^{-1}\) (Table 2, Fig. 4 and S34, ESI†).

The successive, well seen bands with maxima at 18 850 cm\(^{-1}\) (1a) and 18 650 cm\(^{-1}\) (2a) are correlated with spin-allowed transition to \(^4\)E state being one of the two components of parental

Fig. 4 The NIR-Vis-UV diffuse-reflectance electronic spectra of 1a, 2a and H\(_4cppZol\), H\(_4cbtZol\) ligands (Scheme 1) obtained at room temperature.

Table 2 Band assignments, experimental and theoretical energies (cm\(^{-1}\)) of components of spin-allowed and spin-forbidden d–d transitions for 1a, 1b and 2a

| Cobalt(ii) complexes (d\(^7\) configuration) | Nickel(ii) complex (d\(^8\) configuration) |
|---------------------------------------------|------------------------------------------|
| Assignment | 1a | 2a | Assignment | 1b | 2a |
| \(O_h\) | \(D_{1g}\) (F) | \(A_2\) | 0 | 0 | 0 | \(A_{2d}\) (F) | \(B_1\) | 0 |
| \(E\) | 6830 | 6830 | 6734 | 6950 | 6950 | 6629 | \(T_{2g}\) (F) | \(B_2\) | 7000 | 6990 | 6590 |
| \(E\) (G) | 8250 | 8250 | 8226 | 8050 | 8050 | 8190 | \(E(1)\) | 8500 | 8370 | 8310 |
| Ligand | 11 300 | 11 350 | 11 300 | 11 350 | 11 300 | 11 275 | - | 11 230 | 11 430 | - |
| \(B_1\) | 12 510 | 12 444 | 12 430 | 12 266 | 12 266 | 12 266 | - | 12 300 | 12 300 | - |
| \(E\) (G) | 13 040 | 13 040 | 13 040 | 13 040 | 13 040 | 13 040 | - | 13 040 | 13 040 | - |
| \(E\) (P) | 19 150 | 19 150 | 19 150 | 19 150 | 19 150 | 19 150 | - | 19 150 | 19 150 | - |
| \(T_{2g}\) (P) | 20 510 | 20 510 | 20 510 | 20 510 | 20 510 | 20 510 | - | 20 510 | 20 510 | - |
| \(A_1\) (G) | 21 310 | 21 650 | 21 741 | 21 490 | 21 520 | 21 520 | - | 21 310 | 21 310 | - |
| \(A_2\) | 21 760 | 21 760 | 21 760 | 21 760 | 21 760 | 21 760 | - | 21 760 | 21 760 | - |
| \(E\) (G) | 24 189 | 24 189 | 24 189 | 24 189 | 24 189 | 24 189 | - | 24 189 | 24 189 | - |
| \(E\) (P) | 24 811 | 24 811 | 24 811 | 24 811 | 24 811 | 24 811 | - | 24 811 | 24 811 | - |
| \(T_{1g}\) (G) | 26 220 | 26 270 | 26 226 | 26 370 | 26 331 | 26 331 | - | 26 220 | 26 220 | - |

a Spect. – the energy found from the experimental spectra; filter – the energy found from the filtering process (filter parameters: (1a) step = 20 cm\(^{-1}\), \(\alpha = 400\) and \(N = 30\); (2a) step = 20 cm\(^{-1}\), \(\alpha = 400\) and \(N = 30\); (1b) step = 20 cm\(^{-1}\), \(\alpha = 300\) and \(N = 30\); calcd – calculated energy; – not observed; the spin-allowed transitions are marked in bold.
The magnetic susceptibilities of 1a, 1b and 2a show Curie–Weiss behaviour above ca. 50 K with the Weiss constants \( \theta = -12.4, -8.3, \) and \(-2.1 \) K, and magnetic moments of 5.32 (2.75), 5.32 (2.75), and 5.32 (2.75), respectively. For cobalt(II) compounds, the tetragonal crystal field parameters \( D_{q1}, D_{q2} \) and \( D_{q3} \) as well as the Racah parameters \( B \) and \( C \) were calculated using the energies of quartet–quartet transitions. The following sets were obtained: \( D_{q1} = 583 \) cm\(^{-1} \), \( D_{q2} = -168 \) cm\(^{-1} \), \( D_{q3} = 568 \) cm\(^{-1} \), \( B = 890 \) cm\(^{-1} \), \( C/B = 4.12 \) (1a) and \( D_{q4} = 572 \) cm\(^{-1} \), \( D_{q5} = -177 \) cm\(^{-1} \), \( D_{q6} = 537 \) cm\(^{-1} \), \( B = 888 \) cm\(^{-1} \), \( C/B = 4.08 \) (2a). The \( D_{t} \) is dependent on the splitting of the first quartet state of the octahedral \( T_{2g}(4P) \) and its negative sing calculated for both 1a and 2a is in agreement with the compressed geometry of \( \{CoO\} \) polyhedrons in \( NaCo_{3}(SeO_{3})(OH)_{4}\) and \( Co_{3}(HepZol)_{3}(H_{2}O)_{4}\) coordination unit. For nickel(II) complex 1b, the values of \( D_{q1}, D_{q2}, D_{q3} \), and Racah parameter \( B \) were calculated using the energies of six-triplet states. The following values were obtained: \( D_{q1} = 659 \) cm\(^{-1} \) (exp. energy 699 cm\(^{-1} \) for \( 3B_{1} \rightarrow 3B_{2} \) transition, Table 2), \( D_{q2} = 307 \) cm\(^{-1} \), \( D_{q3} = -196 \) cm\(^{-1} \) and \( B = 932 \) cm\(^{-1} \).
5.23 (2.70), and 3.34 (2.30) \( \mu_B \), respectively. The expected values for \( g \) factors corresponding to the respective moments for free Co(II) (1a, 2a) or Ni(II) (1b) ions are given in brackets. Full results of magnetic measurements and calculations are presented in Fig. S36–S39 (ESI†). The magnetic behaviours of 1a and 2a are very similar, therefore Fig. 6 presents the temperature dependence of the effective magnetic moments (\( m_{\text{eff}} \)) only for 1a and 1b. The magnetic susceptibilities of both compounds increase monotonically as the temperature is decreased up to 1.7 K. Upon cooling, the effective magnetic moment of Co(II) complex 1a slightly decreases from 300 to 100 K and then decreases faster, reaching a value of 4.1 \( \mu_B \) at \( ~2 \) K. An effective moment of the nickel complex 1b slowly decreases below room temperature, reaches a shallow minimum at 55 K, then passes through a pronounced maximum at 5 K and drops sharply below this temperature.

The crystals structures of all the compounds comprise zigzag chains, in which metal centres are alternately linked by double, symmetrical \((-O1-P1-O2-)_2\) and \((-O4-P2-O6-)_2\) bridges (Fig. S8†). Therefore, the magnetic susceptibility of 1a, 2a and 1b was analyzed in the framework of an alternating-exchange spin-chain.

Using the Hamiltonian:

\[
H = -J_1 \sum S_i S_{i+1} - J_2 \sum S_{i+1} S_{i+2}
\]

Cortés\(^{40}\) has derived the exact expression for magnetic susceptibility of \( J_1J_2 \) alternating chain with Heisenberg-type exchange between the classical spins:

\[
\chi_{\text{alt}} = N\beta^2g^2S(S+1)/3k_B T \cdot F_{\text{alt}}
\]

\[
F_{\text{alt}} = (1 + u_1 + u_2 + u_1u_2)/(1 - u_1u_2)
\]

where \( u_i = \coth[J_iS(S + 1)/k_B T] - k_B T/J_iS(S + 1) \) and \( N, \beta, g, \) and \( k_B \) have their usual meanings.

If the antiferromagnetic coupling is weak or its character is ferromagnetic, the influence of zero-field splitting (zfs) must be taken into account in an analysis of the magnetic behaviour at low temperatures. The bulk susceptibility of 1a, 2a and 1b was calculated in the full temperature range by the combination of zfs and the alternating chain\(^{41-43}\) as:

\[
\chi = \chi_{\text{zfs}} F_{\text{alt}} + \text{TIP}.
\]
According to Boca, the zfs contribution can be represented by

\[
\chi_{\text{zfs}} = (\chi_{\parallel} + 2 \chi_{\perp})/3
\]

where:

\[
\chi_{\parallel} = (N\beta^2 g_{\parallel}^2/k_B T)\left(1 + 9d^2\right) / (1 + d^2),
\]

(5a)

\[
\chi_{\perp} = (N\beta^2 g_{\perp}^2/k_B T)\left[1 + 3k_B T/4D \cdot (1 - d^2)\right](1 + d^2),
\]

(5b)

for the cobalt compounds (1a, 2a) or:

\[
\chi_{\parallel} = (N\beta^2 g_{\parallel}^2/k_B T)2d(1 + 2d),
\]

(6a)

\[
\chi_{\perp} = (N\beta^2 g_{\perp}^2/k_B T)2k_B T/4D \cdot (1 - d^2)(1 + 2d)
\]

(6b)

for the nickel compound (1b), D is the axial zfs parameter and
d = e^{−D/k_BT}. In order to avoid overparametrization, isotropic g values were assumed.

The best agreement between theory and experiment was obtained for \(J_1 = -0.72, -1.07, -2.47\) cm\(^{-1}\), \(J_2 = 0.33, 0.42, 0.67\) cm\(^{-1}\), \(D = 58.2, 51.4, -1.86\) cm\(^{-1}\), \(g = 2.69, 2.67, 2.25\), and

\[
R \text{ defined as } \frac{\Sigma(x[T]_{\text{exp}} - (x[T]_{\text{calc}})^2)}{\Sigma(x[T]_{\text{exp}}^2)} \text{ equal to } 6.2 \times 10^{-5}, 5.6 \times 10^{-5}, 7.8 \times 10^{-6}\text{, for 1a, 2a and 1b, respectively. During the calculations, the temperature independent paramagnetism (TIP) was fixed at } 60 \times 10^{-6} \text{ emu per Co. Good fit of calculated and experimental values of magnetic susceptibility of 1b at temperatures above 100 K could be achieved with a TIP value of 201 \times 10^{-6} \text{ emu per Ni. The susceptibility curves resulting from the above parameters (depicted as } \mu_{\text{eff}}(T) \text{ and } \chi^{-1}(T) \text{) are shown in Fig. 6 and S36-S38 (ESI†). Since it is not possible to calculate field dependent magnetization within the above model, we have tried to ignore weak exchange interactions, treating the system as a set of isolated Co(II) ions and leaving the rest of the parameters unchanged. The } M(\beta) \text{ dependences calculated for various external fields are drawn in Fig S39 (ESI†) as a solid line and fit the experimental data pretty well.}

The magnetic susceptibility of cobalt compounds calculated in the zero magnetic field using formulas 2–5 does not depend on the sign of the D parameter. In strong magnetic fields (above 0.5 T) a significant difference between the magnetization calculated for D and −D is observed (Fig. S39, ESI†) with a clear indication of positive values. This corresponds to the compressed tetragonal bipyramid around the cobalt centres (Fig. 1) and is consistent with the results of the analysis of the electronic spectra of 1a and 2a. It is also possible to fit the temperature dependence of magnetic susceptibility using both positive and negative values of parameter D for the nickel compound (1b). However, in this case the set of selected parameters with negative D (which again corresponds to the compressed bipyramid) better describes the behaviour of magnetization as a function of the magnetic field (Fig S39, ESI†).

Although coordination compounds containing various metal centres connected by −O−P−O− bridges are quite common and the magnetic properties of many of them have been investigated, a question still arises about the nature of magnetic exchange couplings through −O−P−O− bridges. Correlations of exchange integrals with M−O−P−O dihedral angles (related to deviation of the phosphonate group from the mean M−O−O−M plane) or with the angle between the O−P−O plane and the M−O axis, supported by the DFT calculations suggest that the most important structural parameter controlling the exchange coupling is the M−O−O−M dihedral angle over the O−P−O bridge. The antiferromagnetic coupling decreases with the increase of the M−O−O−M angle and the coupling can become ferromagnetic in the case of larger angles. The \(J\) values calculated for 1a, 2a and 2b can readily be rationalized in terms of magnetostuctural correlations outlined above. For both 1a and 2a, the boundary between ferro- and antiferromagnetic couplings estimated by this method for Co−O−O−Co angle is ca. 80°, and as seen in Fig. S40 and Table S7 (ESI†), the same observation seems to be applicable for 1D Co_{2}(HL)_{2}(H_{2}O)$_6$ polymers featuring chains of linear symmetric Co2 Co1 Co2 trimers [HL = HdmtZol\(^{3−}\), HeppZol\(^{3−}\), HcbtZol\(^{3−}\), Scheme 1]. Moreover, the same value can also be used to explain magnetic behaviour of 1b and recently reported Ni$_3$(HdmtZol)$_2$(H$_2$O)$_6$ complex.\(^4\)

4. Conclusions

Three Co(II) and Ni(II) 1D coordination polymers based on zoledronic acid analogues with a cyclopropane (cpp) or cyclobutane (cbt) ring on the C\(_8\) carbon, namely [Co(H$_2$cppZol)(H$_2$O)]$\cdot$H$_2$O (1a), [Ni(H$_2$cppZol)(H$_2$O)]$\cdot$H$_2$O (1b) and [Co(H$_2$cbtZol)(H$_2$O)]$\cdot$H$_2$O (2a), were synthesized under hydrothermal conditions and characterized by means of single-crystal X-ray diffraction, spectroscopic and thermal techniques. The studied compounds exhibit 1D double zigzag chains architecture with the 8 + 8 rings motif formed by alternately arranged symmetrical (−O−P−O−)$_2$ bridges linking equivalent octahedral Co(II)/Ni(II) centres.

All the compounds exhibit similar decomposition pathways upon heating with thermal stabilities decreasing in the order 1b > 1a > 2a. The IR spectra revealed that lattice water release does not change chains architecture leaving them intact up to ca. 320, 280 and 240 °C, respectively. A good correlation between calculated energies of d−d transitions and experimental NIR/UV/VIS spectra was obtained with the assumption that metal centres of 1a, 1b and 2a adopt pseudo-octahedral compressed geometry.

Variable temperature magnetic susceptibility measurements analyzed in the framework of an alternating-exchange spin-chain revealed the occurrence of weak alternating antiferromagnetic–ferromagnetic exchange interactions propagated between the magnetic centres along double (−O−P−O−)$_2$ bridges with \(J_1 = -0.72, -1.07, -2.47\) cm\(^{-1}\) and \(J_2 = 0.33, 0.42, 0.67\) cm\(^{-1}\) for 1a, 1b and 2a respectively. The boundary between antiferro- and ferromagnetic couplings for Co−O−O−Co angle was established to be ca. 80°. This value can also be used to explain magnetic behaviour of 1b and is applicable for recently reported M$_3$(HL)$_2$(H$_2$O)$_6$ complexes based on 5,6-disubstituted analogues of zolezadric acid.

Conflicts of interest

There are no conflicts to declare.
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