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Title: Four organo-templated structures with DFT-zeotype topology: variation in symmetry of similar microporous structures

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Corresponding Author: Dr. Tamara Djordjevic, Dr.rer.nat.

Corresponding Author's Institution: Universität Wien

First Author: Ljiljana Karanović

Order of Authors: Ljiljana Karanović; Sabina Kovač; Dejan Poleti; Tamara Djordjevic, Dr.rer.nat.

Abstract: Four novel microporous compounds $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{ZnAsO}_4)_2$ (1), $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{Co}_{0.1}\text{Zn}_{0.9}\text{AsO}_4)_2$ (2), $\text{H}_{1.8}(\text{C}_2\text{H}_8\text{N}_2)(\text{Fe}_{0.1}\text{Zn}_{0.9}\text{AsO}_4)_2$ (3) and $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{ZnPO}_4)_2$ (4) containing ethylenediammonium cation, $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)^{2+}$ (H_2en^{2+}), and ethylenediamine molecule, $\text{C}_2\text{H}_8\text{N}_2$ (en), have been hydrothermally synthesized. While 1-3 exhibit twinned DFT-zeotype structure and crystallize in $\text{P}4_2/\text{n}$, the 4 is characterized by the appearance of new orthorhombic space group Pcca , previously not observed among the known DFT-zeotype compounds. The symmetry relationships analyses revealed the extended Bärnighausen tree. The main feature of the cobalt blue and reddish brown compounds 2 and 3 is their novel chemical composition which was confirmed by SEM/EDX analysis. In the structure of 1, H-atoms positions, previously not reported, were calculated and refined to reasonable positions using riding model. The DFT anionic frameworks of 1-4 are characterized by 4M, 6M and 8M tetrahedral rings, which produce three mutually perpendicular 8M ring channels. At the intersections of these channels H_2en^{2+} cations are accommodated and hydrogen-bonded to the adjacent oxygen atoms of the framework. Only in 3, H_2en^{2+} is partly substituted by electroneutral en to maintain charge compensation. The single-crystal Raman spectra and Fourier transform infrared (FTIR) absorption spectra were interpreted on the basis of characteristic vibrations of AsO_4 and PO_4 groups, as well as of NH_3 , NH_2 and CH_2 groups from the H_2en^{2+} cation or en molecule. The results of lattice distortion and similarity analyses showed that the DFT-zeotype structures, which incorporate larger tetrahedral cations, have a higher degree of lattice distortion and are less similar to the ideal structural models derived from the aristotype.

universität
wien

Fakultät für Geowissenschaften,
Geographie und Astronomie

Dr. Tamara Đorđević
Institut für Mineralogie und
Kristallographie
Althanstraße 14
A-1090 Wien

T +43 (1) 4277-532 0139
F +43 (1) 4277-95 32
Mineralogie@univie.ac.at

To:
Prof. Dr. Wolfgang Schmidt
Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1
D-45470 Mülheim an der Ruhr

Wien, am 09.04.2015

Dear Prof. Schmidt,

please find enclosed a manuscript entitled: "Four organo-templated structures with DFT-zeotype topology: variation in symmetry of similar microporous structures" which we would like to have considered for publication in the Microporous and Mesoporous Materials.

In the manuscript mentioned above, we report hydrothermal synthesis, structure determination, Raman and infrared spectra of four novel microporous compounds $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{ZnAsO}_4)_2$ (**1**), $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{Co}_{0.1}\text{Zn}_{0.9}\text{AsO}_4)_2$ (**2**), $\text{H}_{1.8}(\text{C}_2\text{H}_8\text{N}_2)(\text{Fe}_{0.1}\text{Zn}_{0.9}\text{AsO}_4)_2$ (**3**) and $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{ZnPO}_4)_2$ (**4**) containing ethylenediammonium cation, $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)^{2+}$ (H_2en^{2+}), and ethylenediamine molecule, $\text{C}_2\text{H}_8\text{N}_2$ (en). While **1-3** exhibit twinned DFT-zeotype structure and crystallize in tetragonal $P4_2/n$ space group, the structure of **4** is characterized by the appearance of new orthorhombic space group *Pcca*, previously not observed among the known compounds with DFT-zeotype framework topology. An analyses of the symmetry relationships between all members known until now was undertaken. The results of this analysis revealed the extended Bärnighausen tree. The emphasis was placed on the novel orthorhombic space group *Pcca*. The main feature of the cobalt blue and reddish brown compounds **2** and **3** is their novel chemical composition and occurrence of one mixed tetrahedral position occupied by Zn/Co and Zn/Fe, respectively. The presence of Co and Fe cations was confirmed by SEM/EDX analysis. In the structure of **1**, hydrogen atoms, previously not reported in the structure of the compound with identical chemical composition, were calculated and refined to reasonable positions using riding model.

The DFT anionic frameworks of **1-4** are built from alternating tetrahedra: ZnO_4 and AsO_4 in **1**, $(\text{Co}_{0.1}\text{Zn}_{0.9})\text{O}_4$ and AsO_4 in **2**, $(\text{Fe}_{0.1}\text{Zn}_{0.9})\text{O}_4$ and AsO_4 in **3**, ZnO_4 and PO_4 in **4**. They are linked through their vertices generating 4M, 6M and 8M tetrahedral rings, which produce three mutually perpendicular 8M ring channels. At the intersections of these channels H_2en^{2+} cations are accommodated and hydrogen-bonded to the adjacent oxygen atoms of the framework. Only in **3**, H_2en^{2+} is partly substituted by electroneutral en to maintain charge compensation. The single-crystal Raman spectra and Fourier transform infrared (FTIR) absorption spectra were interpreted on the basis of characteristic vibrations of AsO_4 and PO_4 groups, as well as of NH_3 , NH_2 and CH_2 groups from the H_2en^{2+} cation or en molecule.

In order to analyze the structure distortion involved, the comparison of ideal (derived from aristotype) and real (obtained from experimental data) structural models were made using the program COMPSTRU hosted in the Bilbao Crystallographic Server (<http://www.cryst.ehu.es>). It was found that the DFT structures, which incorporate larger tetrahedral cations, have a higher degree of lattice distortion and are less similar to the ideal structural models derived from the aristotype.

The manuscript has not been previously published or submitted for publication to another journal. The research was carried out in the collaboration with Ljiljana Karanović, Sabina Kovač and Dejan Poleti from University of Belgrade, Serbia, who all approved the submission of the paper to the Microporous and Mesoporous Materials in the present form.

Sincerely,
Tamara Đorđević

1. Prof. Dr. Wolfgang Schmidt
Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1
D-45470 Mülheim an der Ruhr
tel +49(0)208/306-2370
fax +49(0)208/306-2995
e-mail: schmidt@mpi-muelheim.mpg.de
e-mail: wolfgang.schmidt@kofo.mpg.de

2. Dr. Stanislav Lazarov Ferdov
Universidade do Minho, Departamento de Física,
Campus de Azurém, 4800-058 Guimarães
Portugal
tel +351 253510468
fax + 351 253 510461
e-mail: sferdov@fisica.uminho.pt

3. Prof. Dr. Sergey Krivovichev
Department of Crystallography,
Faculty of Geology
St. Petersburg State University,
University Emb. 7/9
199034, St. Petersburg,
Russia
Tel: +7 812 350 66 88
e-mail: skrivovi@mail.ru

Highlights

- Single crystals of $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{ZnAsO}_4)_2$ (**1**), $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{Co}_{0.1}\text{Zn}_{0.9}\text{AsO}_4)_2$ (**2**), $\text{H}_{1.8}(\text{C}_2\text{H}_8\text{N}_2)(\text{Fe}_{0.1}\text{Zn}_{0.9}\text{AsO}_4)_2$ (**3**) and $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{ZnPO}_4)_2$ were grown using hydrothermal technique
- **1-3** exhibit twinned DFT-zeotype structure and crystallize in space group $P4_2/n$
- **4** is characterized by the appearance of new orthorhombic space group $Pcca$, previously not observed among the known compounds with DFT-zeotype framework topology
- Analyses of the symmetry relationships between all compounds adopting DFT-zeotype topology was undertaken
- Structure distortion using the program COMPSTRU was analyzed

Four organo-templated structures with DFT-zeotype topology: variation in symmetry of similar microporous structures

Ljiljana Karanović^a, Sabina Kovač^a, Dejan Poleti^b, Tamara Đorđević^{c,*}

^aLaboratory for Crystallography, Faculty of Mining and Geology, University of Belgrade, Đušina 7, 11000 Belgrade, Serbia

^bFaculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia

^cInstitut für Mineralogie und Kristallographie-Geozentrum, Universität Wien, Althansstr. 14, A-1090 Wien, Austria

*Corresponding author:

Tamara Đorđević, Tel: (+43-1) 4277 - 53239, Fax: (+43-1) 4277 - 9532,

e-mail: tamara.djordjevic@univie.ac.at

E-Mail addresses of all authors:

Ljiljana Karanović: ljika2002@yahoo.com

Sabina Kovač: sabinakovac@yahoo.com

Dejan Poleti: dejan@tmf.bg.ac.rs

Abstract

Four novel microporous compounds $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{ZnAsO}_4)_2$ (**1**), $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{Co}_{0.1}\text{Zn}_{0.9}\text{AsO}_4)_2$ (**2**), $\text{H}_{1.8}(\text{C}_2\text{H}_8\text{N}_2)(\text{Fe}_{0.1}\text{Zn}_{0.9}\text{AsO}_4)_2$ (**3**) and $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{ZnPO}_4)_2$ (**4**) containing ethylenediammonium cation, $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)^{2+}$ (H_2en^{2+}), and ethylenediamine molecule, $\text{C}_2\text{H}_8\text{N}_2$ (en), have been hydrothermally synthesized. While **1-3** exhibit twinned DFT-zeotype structure and crystallize in $P4_2/n$, the **4** is characterized by the appearance of new orthorhombic space group $Pcca$, previously not observed among the known DFT-zeotype compounds. The symmetry relationships analyses revealed the extended Bärnighausen tree. The main feature of the cobalt blue and reddish brown compounds **2** and **3** is their novel chemical composition which was confirmed by SEM/EDX analysis. In the structure of **1**, H-atoms positions, previously not reported, were calculated and refined to reasonable positions using riding model.

The DFT anionic frameworks of **1-4** are characterized by 4M, 6M and 8M tetrahedral rings, which produce three mutually perpendicular 8M ring channels. At the intersections of these channels H_2en^{2+} cations are accommodated and hydrogen-bonded to the adjacent oxygen atoms of the framework. Only in **3**, H_2en^{2+} is partly substituted by electroneutral en to maintain charge compensation. The single-crystal Raman spectra and Fourier transform infrared (FTIR) absorption spectra were interpreted on the basis of characteristic vibrations of AsO_4 and PO_4 groups, as well as of NH_3 , NH_2 and CH_2 groups from the H_2en^{2+} cation or en molecule.

The results of lattice distortion and similarity analyses showed that the DFT-zeotype structures, which incorporate larger tetrahedral cations, have a higher degree of lattice distortion and are less similar to the ideal structural models derived from the aristotype.

Key words: DFT-zeotype topology; zincoarsenates; zincophosphates, space-group symmetry; single-crystal X-ray analysis

1. Introduction

The open-framework zincoarsenates and zincophosphates are of considerable interest for catalysis, as adsorbents and are promising materials for a wide variety of other applications as a result of their microporous structure, good thermal and acid stability [1]. The flexibility of the DFT-zeotype framework leads to quite different chemical compositions and symmetries (Table 1). One of the interesting features of this group of compounds is that the individual members, although having an identical chemical composition, can adopt several different space groups. Baur and Fischer [2] reported the symmetry relationship between six previously known members of DFT-zeotype compounds (compounds from the references 4, 5, 9, 11, 17 and 18 in the Table 1). Recently, these microporous materials have extended their range of compositions and space group symmetries and the current list count 18 members. Their unit cell data, chemical formula, references and some additional data are listed in Table 1.

The aristotype, *i.e.* the space group of the highest topological symmetry, of DFT-zeotype framework is $P4_2/mmc$ (No. 131) [3]. All previously synthesized compounds crystallize as the tetragonal, orthorhombic or monoclinic hettotypes *i.e.* with lower symmetry and larger unit cells than aristotype (Table 1). We have identified four different space groups for known compounds with DFT-zeotype topology: two tetragonal $P4_2bc$ and $P4_2/n$, one orthorhombic $Pccn$, and one monoclinic $C2/c$ (Table 1). Recently, Liu and coworkers [4] have published some observations on powder diffraction data of $H_2(C_2H_8N_2)(ZnPO_4)_2$. They found it isostructural with $H_2(C_2H_8N_2)(ZnPO_4)_2$ reported by Jones and coworkers [5].

An ideal formula for the compounds with DFT-zeotype structure can be written as $H_2en(TT'O_4)_2$. The chemical composition of a framework is $(TT'O_4)_2$, where T are divalent and/or trivalent larger tetrahedral cations (Al^{3+} , Co^{2+} , Fe^{2+} , Ga^{3+} , Mg^{2+} , Zn^{2+}) and T' are tetrahedral cations of smaller radii and higher oxidation states, like P^{5+} , As^{5+} , Ge^{4+} , Si^{4+} .

Therefore, as long as the charge of $T+T'$ is 8+, the DFT framework is neutral. If the charge of tetrahedral cations is less than 8+, the framework has a negative charge which is balanced by the positive charges of H_2en^{2+} . All DFT-zeotype structures contain H_2en^{2+} as the organic template. In **3**, H_2en^{2+} is partly substituted by electroneutral en to maintain charge compensation. The lowest topological symmetry for the DFT framework is monoclinic, where no disorder of H_2en^{2+} was observed due to the symmetry requirements. In all crystal structures of the DFT compounds known so far, TO_4 and $T'O_4$ tetrahedra are considered to be strictly alternating in the frameworks, except for the gallogermanate where Ga and Ge could not be distinguished in the framework [6].

It is interesting to notice that the chemically and structurally very similar compound $(C_3H_{12}N_2)(ZnPO_4)_2$, incorporates diprotonated propylenediammonium cations (1,3-diaminopropane) and crystallizes in monoclinic space group $P2_1$, but does not correspond to DFT-zeotype topology [7].

In the course of the structural investigations of open-framework zincoarsenates and zincophosphates ([8] and references therein), we have synthesized four new compounds $H_2(C_2H_8N_2)(ZnAsO_4)_2$ (**1**), $H_2(C_2H_8N_2)(Co_{0.1}Zn_{0.9}AsO_4)_2$ (**2**), $H_{1.8}(C_2H_8N_2)(Fe_{0.1}Zn_{0.9}AsO_4)_2$ (**3**) and $H_2(C_2H_8N_2)(ZnPO_4)_2$ (**4**) with DFT-zeotype structure. Despite the fact that all four presently investigated compounds adopt DFT-zeotype framework, with H_2en^{2+} as a guest species, they crystallize in two different space groups. In order to investigate the details about symmetry relationships among the various compounds adopting DFT-zeotype structures, and changes in the atomic positions, which determine crystal structures having different space-group symmetries, we undertook the synthesis and structure determinations of **1-4**, although the structures of chemically identical compounds to **1** and **4** were previously reported.

2 Experimental

2.1 Materials

The materials used were: $5\text{ZnO}\cdot 2\text{CO}_3\cdot 4\text{H}_2\text{O}$ (Alfa Products, >99%), $3\text{As}_2\text{O}_5\cdot 5\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$ (Loba Chemie, >99%), $\text{Co}(\text{OH})_2$ (Aldrich, 95%), Fe_2O_3 (Merck, 99%), ethylenediamine (Alfa Aesar, 99%).

2.1.1 Preparation of 1

The compound **1** was synthesized under hydrothermal conditions using $5\text{ZnO}\cdot 2\text{CO}_3\cdot 4\text{H}_2\text{O}$ and $3\text{As}_2\text{O}_5\cdot 5\text{H}_2\text{O}$ as the sources of Zn and As, respectively, whereas ethylenediamine (en) was used as a structure-directing agent. The starting mixture was: 0.2471 g of $5\text{ZnO}\cdot 2\text{CO}_3\cdot 4\text{H}_2\text{O}$ (0.412 mmol), 0.2031 g of $3\text{As}_2\text{O}_5\cdot 5\text{H}_2\text{O}$ (0.260 mmol) and 0.1 ml of en (1.5 mmol). The powder mixture was transferred into Teflon vessel and filled to approximately 70% of its volume with distilled water. The initial pH value of the mixture was 3. The stainless-steel autoclave was then closed and the crystallization was carried out by placing the autoclave in an air oven and heating the mixture under autogenous pressure from room temperature to 433 K for 4 h, held at this temperature for 72 h and cooled to room temperature over a period of 96 h. The pH value of supernatant solution was also 3. The products obtained were washed with distilled water, filtered and dried in the air at room temperature. The compound crystallized as colorless transparent octahedron-like crystals (yield *ca.* 10 %) together with transparent needles of $\text{Zn}_2(\text{As}_2\text{O}_7)(\text{H}_2\text{O})_2$. The maximal size of crystals was about 0.3 mm.

2.1.2 Preparation of 2

The compound **2** was synthesized essentially in the same way as compound **1** using $5\text{ZnO}\cdot 2\text{CO}_3\cdot 4\text{H}_2\text{O}$, $3\text{As}_2\text{O}_5\cdot 5\text{H}_2\text{O}$ and $\text{Co}(\text{OH})_2$ as the sources of Zn, As and Co,

respectively, whereas ethylenediamine (en) was used as a structure-directing agent. The starting mixture was: 0.2030 g $5\text{ZnO}\cdot 2\text{CO}_3\cdot 4\text{H}_2\text{O}$ (0.339 mmol), 0.2753 g $3\text{As}_2\text{O}_5\cdot 5\text{H}_2\text{O}$ (0.353 mmol), 0.1237 g $\text{Co}(\text{OH})_2$ (1.331 mmol) and 0.15 ml en (2.25 mmol). After the addition of distilled water to the mixture, the initial pH value was 7. The crystallization was performed in the same way and at the same temperature as the preparation of **1**. The resulting products were dry at the end of the reaction, which indicates that the autoclave was not tightly closed. The products obtained were washed with distilled water, filtered and dried in the air at room temperature. The compound crystallized as prismatic cobalt blue transparent crystals (yield *ca.* 20 %). The crystals color ranges from shades of light to dark blue. The maximal size of the crystals was about 0.2 mm.

2.1.3 Preparation of **3**

Basically similar procedure was performed to synthesize the compound **3** using $5\text{ZnO}\cdot 2\text{CO}_3\cdot 4\text{H}_2\text{O}$, $3\text{As}_2\text{O}_5\cdot 5\text{H}_2\text{O}$ and Fe_2O_3 as the sources of Zn, As and Fe, respectively, and ethylenediamine (en) was used as a structure-directing agent. The starting mixture was: 0.1514 g $5\text{ZnO}\cdot 2\text{CO}_3\cdot 4\text{H}_2\text{O}$ (0.253 mmol), 0.2097 g $3\text{As}_2\text{O}_5\cdot 5\text{H}_2\text{O}$ (0.269 mmol), 0.1524 g Fe_2O_3 (0.954 mmol), and 0.1 ml en (1.5 mmol). After the addition of distilled water, the initial pH value of the mixture was 6. The crystallization was performed in the same way at 443 K for 4 h, held at this temperature for 72 h and cooled to room temperature over a period of 96 h. The resulting products were dry as in **3**, indicating not tightly closed autoclave. The products obtained were washed out with distilled water, filtered and dried in the air at room temperature. The compound crystallized as prismatic transparent crystals (yield *ca.* 30 %) in different shades of reddish brown. The maximum size of the crystals was about 0.2 mm.

2.1.3 Preparation of **4**

The compound **4** was synthesized from: 0.2348 g $5\text{ZnO}\cdot 2\text{CO}_3\cdot 4\text{H}_2\text{O}$ (0.392 mmol), 0.2137 g $(\text{NH}_4)_2\text{HPO}_4$ (1.618 mmol) and 0.05 ml en (0.749 mmol). The initial pH value of the mixture was 9, after the addition of distilled water. The crystallization was performed using the same conditions as by preparation of **1** and **2**. The pH value of supernatant solution was 7. The products obtained were washed with distilled water, filtrated and dried in the air at room temperature. The compound crystallized as prismatic colorless transparent crystals (yield *ca.* 50 %). The maximal size of the crystals was about 0.3 mm.

2.2 Characterization

2.2.1 Single crystal X-ray diffraction analyses

The room temperature intensity data of all crystals were collected on a Nonius Kappa CCD single-crystal four-circle diffractometer (MoK α -radiation, graphite monochromator), equipped with a 300 mm diameter capillary-optics collimator. Unit cell parameters were determined with HKL SCALEPACK [9]. A complete sphere of reciprocal space (φ and ω scans) was measured. The intensity data were processed with the Nonius program suite DENZO-SMN [9] and corrected for absorption by the multi-scan method [9,10].

All structures were solved by direct methods using SIR97 [11] and refined on F^2 by full-matrix least-squares using SHELXL97 [12] and WinGX [13].

The crystal structures of **1-3** showed twinning by rotation and were solved and refined in the tetragonal space group $P4_2/n$ from twinned single crystals, with an almost equal volume ratio between the two domains (the refined BASF parameters were 0.5175(8), 0.443(1) and 0.608(1) for **1**, **2** and **3**, respectively). The twofold twin axis is along the crystallographic [100] direction, *i.e.* the twin law was defined by the twin matrix $\begin{pmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}$ in all three crystals. The tetrahedral site, T12 in **2** and **3** was refined

as a mixed Zn12/Co12 and Zn12/Fe12 site, respectively, constrained to full occupancy. The identical fractional coordinates and atomic displacement parameters for both atoms in the mixed sites were applied. The identical site occupancies of 0.91(1) and 0.09(1) were obtained for Zn12 and Co12 as well as for Zn12 and Fe12, respectively.

Although the chemical composition of **4** appears to be identical to the $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{ZnPO}_4)_2$, reported by Jones and coworkers [5] in the space group $P4_2bc$ and later in the space group $P4_2/n$ by Pan and Yang [14], it was not possible to refine the structure in the reported space groups. Attempts to refine in the other space groups always resulted in higher R values with unrealistic interatomic bond distances. According to the systematic extinctions and the results of refinement, the orthorhombic $Pcca$ was found as the most suitable.

All non-hydrogen atoms were refined anisotropically. All H atoms were placed in geometrically ideal positions and were refined using the riding model, with fixed atomic displacement parameters $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ and $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{N})$. The C–H and N–H distances were constrained to 0.97 and 0.89 Å, respectively. Selected crystal and experimental data are given in Table 2. The final atomic coordinates and anisotropic displacement parameters are given in Tables 3 and 4, respectively. The selected bond distances and bond angles are listed in Table 5, and hydrogen bonding geometry in Table 6. The results of bond-valence calculations are given in Table 7. All drawings of crystal structures were produced with ATOMS [15].

2.2.2 Scanning electron microscopy (SEM/EDX)

Semiquantitative chemical analysis, which was performed using a JEOL JSM-6610 LV scanning electron microscope (SEM) connected with an Oxford INCA Energy 350 EDX analysis unit, confirmed the presence of Zn and Co in **2** as well as Zn and Fe in **3**. While the crystals of **2** (0.05-0.10 mm in size) were essentially homogeneous, the crystals

of **3** (0.05-0.20 mm in size) appeared inhomogeneous in EDX images (Fig. 1). The measured dopant concentrations in **2** are somewhat smaller than the value observed by XRD, implying various chemical compositions of different single crystals. The Fe doped crystals of **3** had an inhomogeneous appearance even after surface layers were removed (Fig. 1). In spite of differences in the local chemical composition, the ratio of As:(Zn+Fe) in **3** has been preserved close to 1 (ranged from 1.1 to 0.9), while the ratio of As:(Zn+Co) in **2** is somewhat higher than 1 (ranged from 1.1 to 1.3).

2.2.3 Fourier transform infrared and Raman spectra

The single crystal Raman spectra of **1** and **4** were collected using a Horiba LabRam HR Evolution system equipped with a Si-based, Peltier-cooled CCD detector in the spectral range of 4000-100 cm^{-1} . The **2** and **3** shows strong luminescence effect and their Raman spectra were not recorded. The 633 nm excitation line of a He-Ne laser was focused with a 100 $\times$ objective on the randomly oriented single crystals. The sample spectra were acquired with a nominal exposure time of 2×2.5 s (confocal mode, Olympus 1800 lines/mm, Si-based, 1.5 μm lateral resolution, approximately 3 μm depth resolution).

Fourier transform infrared (FTIR) absorption spectra of **2** and **3** were recorded using a Bruker Tensor 27 FTIR spectrophotometer, equipped with mid-IR Globar light source and KBr beam splitter, attached to a Hyperion 2000 FTIR microscope with liquid nitrogen-cooled mid-IR, broad-band MCT detector. A total of 128 scans were accumulated between 4000 and 370 cm^{-1} using the samples prepared as KBr micro-pellets.

3 Results and Discussion

3.1 Description of the crystal structures

The tetragonal aristotype of the DFT-zeotype structure (s.g. $P4_2/mmc$) forms an undistorted framework of corner-sharing tetrahedra (Fig. 2.a). This framework can be build either by the construction of the cross-linked bifurcated hexagonal-square (bhs) chains (Fig. 2.b) or by the perpendicular connection of the 2D 4.8^2 nets number 38 proposed by Smith [16] (Fig. 2.c). The asymmetric unit contains one tetrahedral cation $T1$ and three oxygen atoms: $T1$ at $8p$, $O1$ at $8n$, $O2$ at $4m$ and $O3$ at $4i$ Wyckoff positions. The unit cell parameters of this hypothetical structure are: $a = 7.075$ and $c = 9.023$ Å, $V = 451.65$ Å³, $Z = 8$ [3]. In the aristotype structure regular $T1O_4$ tetrahedra are primary building units (PBUs) and are arranged in 4M tetrahedral rings sharing common $O1$ atoms. The apices of the tetrahedra ($O2$ atoms) in the 4M ring are pointing up and down alternatively (Fig. 2.d). The $T1-O1-T1$ angle in the 4M ring is 145° . These single 4M tetrahedral rings are the secondary building units (SBUs).

The compounds **1-4** possess the same topology as the tetragonal aristotype but crystallize in two different space groups due to structural distortion, which are illustrated in the figures 3-6. Because **1-3** have very similar structures, only **1** and **4** are compared in these figures. The structural distortion is associated with lowering of symmetry and proper cell multiplication. The symmetry of **1-3** are still tetragonal (s.g. $P4_2/n$) with double cell size ($a' \approx a-b$, $b' \approx a+b$, $c' \approx c$), while the orthorhombic structure of **4** (s.g. $Pcca$) is strongly pseudo-tetragonal along $[010]$ with four times larger cell volume ($a' \approx 2a$, $b' \approx c$, $c' \approx 2a$, $V' \approx 4V$) than the aristotype. In all tetragonal **1-3**, origin choice 2 is selected for the unit cell in $P4_2/n$. This requires an origin shift of $1/2, 0, 0$ referred to the coordinate system of aristotype.

Two tetrahedra of different size [ZnO_4 and AsO_4 in **1**, $(Co_{0.1}Zn_{0.9})O_4$ and AsO_4 in **2**, $(Fe_{0.1}Zn_{0.9})O_4$ and AsO_4 in **3**, ZnO_4 and PO_4 in **4**] alternated around the 4M tetrahedral rings. The $T-O-T'$ ($T = Zn, Co, Fe$; $T' = As, P$) angles diverge from 145° and vary in the range $127.32(16)$ - $135.80(11)$ in **1**, $127.3(2)$ - $136.16(19)$ in **2**, $127.65(19)$ - $135.85(15)$ in **3**,

and 130.63(12)-142.46(14) ° in **4** (Figs. 3 and 4). However, all tetrahedra in **1-3** are quite regular or only slightly deformed. The average $T-O$ distances (1.931(5) Å in **1**, 1.933(5) in **2**, 1.932(11) in **3**, as well as 1.937(3) and 1.932(4) in **4**) are close to the value of 1.95 Å calculated for Zn–O distance from the sum of effective ionic radii [17]. The average As–O distances of 1.667 (1) in **1**, 1.665 (2) in **2**, 1.665 (4) in **3** and P–O distances of 1.525 (2) and 1.530 (3) Å in **4** are also similar to the calculated values of 1.685 and 1.52 Å, respectively (Table 5).

The distortion of the aristotype 2D 4.8² net is illustrated in Fig. 5 by the deviation of $T'-T-T'$ and $T-T'-T$ angles in the 4M and 8M tetrahedral rings. The geometrical distortion is obviously somewhat different in tetragonal comparing to the orthorhombic structure. The analysis has shown that the geometries of the H_2en^{2+} appear to be relatively undisturbed. The hydrogen bonds listed in Table 6 and bond-valence calculations in Table 7 show that all possible acceptor O atoms participate in hydrogen bonds.

Considering the valence of Zn, Co, As, P and O as +2, +2, +5, +5, –2, respectively, the framework stoichiometry of $(TT'O_4)_2$ produces a net framework charge of –2, which was confirmed by bond valence sum calculations results (Table 7). The negative framework charges are compensated by H_2en^{2+} . In **3**, a small amount of the trivalent iron has been substituted for divalent zinc. It was assumed that the charge balance was accomplished by the substitution of H_2en^{2+} cations by en molecules. This is supported by the larger affinity of smaller Fe^{3+} [$r(Fe^{3+})^{IV} = 0.49$ Å] for the tetrahedral sites than larger Fe^{2+} [$r(Fe^{2+})^{IV} = 0.63$ Å] cation and by the brown-redisch color of the crystals, characteristic for the compounds with Fe^{3+} . Since the 10 % was the amount of Co^{2+} and Fe^{3+} that was observed in the mixed tetrahedral sites of **2** and **3**, the effects of substitutions of Co^{2+} and Fe^{3+} for Zn^{2+} ions with similar ionic radii [$r(Zn^{2+})^{IV} = 0.60$, $r(Co^{2+})^{IV} = 0.58$, $r(Fe^{3+})^{IV} = 0.49$ Å in tetrahedral sites [17] on the interatomic distances was practically undetectable for X-ray structure analysis.

The asymmetric unit of **1-3** is composed of a $(TT'O_4)^-$ anion and a half of a H_2en^{2+} , which are oriented with their molecular axis parallel to $[100]$ and $[010]$ in the 8M channels. The 4-fold rotoinversion axis $\bar{4}$ $(1/4, 1/4, z)$ passes through H_2en^{2+} in both orientations. The nitrogen atoms are ordered because the symmetry elements generate eight N1 atoms in the unit cell. Therefore, each H_2en^{2+} has only one crystallographically unique N1 atom, whereas H atoms of NH_3^+ groups and two CH_2 groups each have two possible locations directed by symmetry with site occupation factors equal to 0.5. This allows the formation of two differently oriented H_2en^{2+} cations and the hydrogen atoms in $N1H_3$ groups are placed in two different sites. The two possible hydrogen bond patterns are shown in Figs. 6.a. and 6.b. The $N1H_3$ groups in **1-3** are hydrogen bonded to all neighboring O atoms, with $N\cdots O$ distances between 2.877(3) and 3.030(4) in **1**, 2.881(5) and 3.036(5) in **2** and 2.891(4) and 3.042(5) Å in **3** (Table 6). The H_2en^{2+} adopts *anti* conformation with a dihedral angles $N1-C1-C2-N1$ of -176.7 , -176.6 and -176.5° , in **1**, **2** and **3**, respectively.

As already mentioned the unit cell of **4** in *Pcca* has four times larger volume than aristotype, which is achieved by a doubling of the tetragonal a_1 and a_2 unit cell axes and retaining the orthorhombic b as long as tetragonal c . This yields four general $8c$ Wyckoff positions for cations, two of which are occupied by P and the other two by Zn (Table 8). In the space group *Pcca*, the centres of all 4M rings are located on the 2-fold axis, while in the centre of 8M rings no symmetry elements are situated. Two crystallographically different H_2en^{2+} are oriented with their molecular axis parallel to the $[100]$ and $[001]$ in 8M channels 1 and 2, respectively (Figs. 6.c. and 6.d). The H_2en^{2+} , situated in the channel 1, is ordered. One half of molecule is symmetrically equivalent of the other half and they are related by the 2-fold rotation axis which is parallel to the $[001]$. The terminal $N1H_3$ groups of this ordered H_2en^{2+} cation in **4** is hydrogen bonded to oxygen atoms with $N\cdots O$ distances of 2.769(3), 2.880(3) and 2.814(3) Å (Table 6). Another H_2en^{2+} , situated in the channel 2, is partly disordered. The nitrogen atoms N21 and N22 are ordered and placed on the already

mentioned 2-fold rotation axis in special $4d$ positions, whereas both C and all H atoms are partly disordered and located in split sites with 50 % occupation. The positional disorder of C and H atoms is directed by the space group symmetry. The hydrogen atoms in N21H₃ and N22H₃ groups of partly disordered H₂en²⁺ cations have at least two possible orientations caused by symmetry (Figs. 6.c, 6.d, Table 6). Considering bond valence calculations and possible rotation, all oxygen atoms from framework can serve as hydrogen bond acceptors in the case of differently oriented N21H₃ and N22H₃ groups with N...O distances between 2.775(2) and 3.168(2) Å. Both H₂en²⁺ cations in **4** also adopt *anti* conformation with dihedral angles N1–C1–C1–N1 and N21–C21–C22–N22 equal to –173.6 and 176.9 °, respectively.

The properties of a porous material are determined by the average porosity of the framework. A measure of the framework porosity is the framework density, defined as the number of tetrahedral atoms per 1000 Å³. The compounds **1-3** with [Zn–As–O], [(Co_{0.1}Zn_{0.9})–As–O] and [(Fe_{0.1}Zn_{0.9})–As–O] frameworks are characterized by the slightly lower framework density (15.50, 15.49 and 15.48 tetrahedral atoms per 1000 Å³, respectively) in comparison to the compound **4** with [Zn–P–O] framework density (16.53 tetrahedral atoms per 1000 Å³), indicating that compounds **1-3** belong to the somewhat more opened structure than **4**. The values of framework densities for known structures with DFT topology are listed in Table 1.

The results of bond-valence calculations [18] confirm the presence of divalent zinc and cobalt with pentavalent arsenic and phosphorus in **1**, **2** and **4** (Table 7). Calculated values range from 2.1 to 2.2 valence units (v.u.) for $\Sigma v_{ij}(T)$ and from 5.1 to 5.3 v.u. for $\Sigma v_{ij}(T')$ where $T = \text{Zn, Co}$ and $T' = \text{As, P}$. Neglecting the contribution from the hydrogen bonds the bond valence sums for the oxygen atoms range from 1.7 to 1.9 v.u. indicating that all O atoms act as hydrogen bond acceptors (Table 7). Because of very small amount of

Fe³⁺ in **3**, the effects of substitutions of Fe³⁺ for Zn²⁺ ions in mixed tetrahedral site on the sum of bond-valences was not possible to detect.

3. 2 Interpretation of the Raman and Infrared spectra

The Raman spectra of **1** and **4** are shown in Fig. 7 while FTIR spectra of **2** and **3** in Fig. 8. Their interpretation can be made on the basis of characteristic vibrations of AsO₄ and PO₄ groups, as well as of NH₃, NH₂ and CH₂ groups from the H₂en²⁺ cation or en molecule. The Raman spectra of **1** and **4** are similar in the high frequency spectral region. Below 1200 cm⁻¹, Raman bands have different positions, due to the difference in vibrational modes of AsO₄³⁻ and PO₄³⁻ ions in **1** and **4**, respectively. The precise assignment of all the bands present in the spectra is difficult, because a large number of observed bands and by the fact that many vibrations due to the different group of atoms fall in the same spectral range. However, by comparing the data reported in the literature [8, 19-21] the distinct frequency ranges may be assigned as follows.

The high frequency spectral region of **1** (from 4000 to 1200 cm⁻¹) shows the NH₃ and CH₂ stretching and bending modes. The peaks at 3016 (vw), 2994(s) and 2981(s) cm⁻¹ in **1** and 3008 (w), 3002 (sh) and 2988 (m) cm⁻¹ in **4** belong to N–H asymmetric and symmetric stretches (ν NH₃). The peaks at 2945 (m), 2923 (w), 2911 (w), 2901 (w) and 2812(w) cm⁻¹ in **1** and 2944 (m), 2909 (m), 2903 (sh), 2822 (w) and 2816 (w) cm⁻¹ in **4** belongs to C–H asymmetric and symmetric stretches (ν CH₂). In the spectral region between 1700-1200 cm⁻¹ appear bands due to the bending modes of the NH₃ and CH₂ groups [δ NH₃: 1639 (vw), 1612(vw), 1534 (w) cm⁻¹ and δ CH₂: 1492 (w), 1480 (m), 1414 (w) cm⁻¹ in **1** and δ NH₃: 1621 (w), 1546 (w) and δ CH₂: 1496 (w), 1486 (sh), 1419 (vw) cm⁻¹ in **4**] followed by the CH₂ torsional modes [τ CH₂: 1348 (vw), 1331 (s), 1271 (w) and 1241 (w) cm⁻¹ in **1** and 1338 (s) and 1281 (vw) cm⁻¹ in **4**]. In **1**, the spectral 1100-600 cm⁻¹ region is due to symmetric and asymmetric stretching region of arsenates. The most intense Raman bands

are observed at 895, 890, 863 and 850 cm^{-1} . In **4**, the Raman bands at 1116 (m), 1071 (s), 1035 (w), 994 (vs), 971 (sh) and 962 (s) cm^{-1} represent stretching frequencies of PO_4 groups. In the region below 700 cm^{-1} , the bending modes of the AsO_4 or PO_4 groups, ZnO_4 vibrations and various lattice modes of the compound **1** and **2** appear.

The FTIR spectra of **2** and **3** compare very well with each other: bands above 3000 cm^{-1} are due to the stretching of the NH_3 group and are present in the infrared spectra of **2** as broad strong peak at 3431 cm^{-1} , followed by two shoulders of medium intensity at 3266 and 3105 cm^{-1} . The C–H stretching appears between 3000-2840 cm^{-1} , with sharp peaks at 2923 and 2853 cm^{-1} in both **2** and **3** spectra. The peaks between 2840-1700 cm^{-1} of weak and medium intensity are due to the overtone and combination bands, and possibly several bands are due to the interaction with the KBr matrix [19 and references therein]. In the spectral region between 1700 and 1200 cm^{-1} appear bands due to the bending modes of the NH_3 and CH_2 groups [δNH_3 : 1649 (s), 1632(sh), 1581(m), 1522 (s) cm^{-1} and δCH_2 : 1468 (w), 1418 (w) cm^{-1} in **2** and δNH_3 : 1652 (w), 1580 (w), 1522 (s) cm^{-1} and δCH_2 : 1469 (w) and 1456 (vw) cm^{-1} in **3**] followed by the CH_2 torsional modes [tCH_2 : 1386 (m), 1362 (w), 1346 (w) and 1242 (w) cm^{-1} in **2** and 1362 (w), 1345 (w) and 1242 (vw) cm^{-1} in **3**]. The bands between 1200-1000 cm^{-1} are due to the rocking modes rNH_3^+ [1127 (m) and 1085 (sh) in **2** and 1127 (m) in **3**] and C–N stretching mode (1059 cm^{-1} in both **2** and **3**). The peaks at 857 (sh), 832 (vs), 796 (sh), 504 (sh), 479 (s) and 460 (sh) in both infrared spectra of **2** and **3**, represent the stretching frequencies of AsO_4 and compare well with the IR spectra of adamite, $\text{Zn}_2(\text{AsO}_4)(\text{OH})$ [20]. Below 750 cm^{-1} the bending modes of the AsO_4 groups, vibrations of ZnO_4 and various lattice modes of the compounds appear.

3. 3 Symmetry relationships among DFT-zeotype structures

The symmetry relationships among DFT-zeotype structures are very complex. In order to explain the supergroup-subgroup relationships between these structures, the

individual ideal models are derived from the aristotype structure. The development of the site relationships from the aristotype to the structures of lower symmetry is given in Table 8. As previously mentioned all known structures have lower symmetries than aristotype, due to ordering of the frameworks tetrahedra and H_2en^{2+} . The symmetry relationships between them (Fig. 9) are represented by the Bärnighausen tree [22], which is more extensive in comparison to the Bärnighausen tree reported earlier by Baur and Fischer [2]. In addition, the transformation of the unit cell is given in Fig. 10 describing the new setting of the unit-cell axes in the subgroup.

3. 4 Structure distortion and the measure of similarity

In order to analyze the structure distortion involved, the comparison of ideal (derived from aristotype) and real (obtained from experimental data) structural models were made using the program COMPSTRU [23] hosted in the Bilbao Crystallographic Server (<http://www.cryst.ehu.es>). It compares two structures that crystallize in the same space group and have atoms occupying the same Wyckoff positions. The difference between them is quantified by the degree of lattice distortion S and the measure of similarity Δ [24], which is zero in the case of complete coincidence. In addition, the maximum distance, d_{max} and the average distance, d_{av} , were calculated (Table 9). The maximum distance, d_{max} , shows the maximal displacement between the atomic positions of the paired atoms. The average distance, d_{av} , is defined as the average of the distances between the atomic positions of the paired atoms over the primitive unit cell. The relative atomic coordinates of the DFT-zeotype structures and corresponding coordinates derived from aristotype with calculated values for S , Δ , d_{max} , and d_{av} are given as Supplementary Material, Table 1S.

It has been shown that the structural changes depend not only on the average ionic radii $(r_T + r_{T'})/2$, but also on the ratio of ionic radii $(r_T / r_{T'})$. A linear dependence with a rather high correlation coefficient R was found for both, the degree of lattice distortion, S

and the measure of similarity, Δ , versus the average ionic radii (Fig. 11). For S vs. $(r_T + r_{T'})/2$ the obtained linear function parameters are $y = -0.031(6) + 0.138(14) \cdot x$, $R = 0.940(2)$ and for Δ vs. $(r_T + r_{T'})/2$ the calculated linear equation is $y = 0.001(13) + 0.268(31) \cdot x$ with $R = 0.929(5)$. The degree of lattice distortion, S , vary from 0.0151 to 0.0370 and it is the smallest for $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{AlSiO}_4)_2$ [1] (Dong *et al.*, 2008) and the largest for $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{ZnAsO}_4)_2$ [25] and **1**, which incorporate a relatively large As. The measures of similarity, Δ , vary from 0.085 to 0.127. As expected, the most similar to the structural model derived from aristotype is $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{AlSiO}_4)_2$ [1], while the structures of $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{ZnAsO}_4)_2$ [25] and **1-3**, which include larger tetrahedral cations, are less similar (Fig. 11).

On the contrary, the dependence of the lattice distortion, S , and the structure similarity, Δ , versus ratio of ionic radii, $r_T / r_{T'}$, are not linearly dependent (Fig. 11). The results can be roughly arranged in four groups. In one group is only $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{AlSiO}_4)_2$ [1] with the lowest values of S and Δ . The S and Δ values, which were obtained for $\text{H}_{1.8}(\text{C}_2\text{H}_8\text{N}_2)(\text{Al}_{0.90}\text{Ge}_{0.73}\text{Si}_{0.37}\text{O}_4)_2$ and $\text{H}_{1.88}(\text{C}_2\text{H}_8\text{N}_2)(\text{Al}_{0.94}\text{Ge}_{0.43}\text{Si}_{0.63}\text{O}_4)_2$ [6] from the next group, were somewhat higher than those obtained for $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{AlSiO}_4)_2$. The highest values of S and Δ were obtained for the structures of $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{ZnAsO}_4)_2$ [25], **1-3**, and $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{GaGeO}_4)_2$ [26], which have $r_T / r_{T'}$ similar to compounds from the two first groups. The other structures belong to the most numerous group with significantly larger ratio of ionic radii, but middle values of S and Δ (Fig. 11).

The $r_T / r_{T'}$ ratio is also reflected in the space group symmetry: the increase in ratio leads to a lower symmetry. When $r_T / r_{T'}$ ratio is between 1 and 2 only structures in $P4_2/n$ were formed. With increasing the $r_T / r_{T'}$ ratio, structures with lower symmetry or evident disorder appear. The decrease of symmetry occurs as a result of rotation of the coordination tetrahedra, which causes the deviations from the ideal structural model derived from aristotype.

It is interesting to emphasize that in all structures the maximal displacement from the ideal positions shows the O2 atoms, *i.e.* the apices of the tetrahedra which link the adjacent 2D 4.8² nets in the 3D framework. The average distances between the atomic positions of the paired atoms are the lowest for two structures with monoclinic symmetry and the highest for arsenates.

4 Conclusion

Due to the framework flexibility, a complete group of compounds, that has been found to adopt DFT-zeotype topology, is characterized by the changes in chemical composition of the open 3D tetrahedral frameworks with the negative net charge balanced by the positive charges of non-framework cations, which are always diprotonated ethylenediamine, H_2en^{2+} .

Although the frameworks of $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{ZnAsO}_4)_2$ (**1**), $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{Co}_{0.1}\text{Zn}_{0.9}\text{AsO}_4)_2$ (**2**), $\text{H}_{1.8}(\text{C}_2\text{H}_8\text{N}_2)(\text{Fe}_{0.1}\text{Zn}_{0.9}\text{AsO}_4)_2$ (**3**) and $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{ZnPO}_4)_2$ (**4**) are built from rather regular or slightly deformed tetrahedra, their structures crystallize in two different space groups. A particularly interesting and unique one is the structure of **4**, which crystallizes in a novel orthorhombic *Pcca*, while the structures of **1-3** crystallize in the most frequent tetragonal *P4₂/n* space group. The crystal structures of **1-3** showed twinning by rotation.

The structure analysis of **1-4** has shown that the geometries of the H_2en^{2+} cations appear to be relatively ordered. Each H_2en^{2+} in **1-3** has only one crystallographically unique N1 atom, whereas H atoms of NH_3^+ groups and two CH_2 groups each have two possible locations directed by symmetry. One of the H_2en^{2+} cations in **4** is ordered and the other is partly disordered similar to structures in the space group *P4₂/n*, *i.e.* the positionally disorder of CH_2 and NH_3^+ groups is caused by the space group symmetry. The hydrogen bonds and

bond-valence calculations show that all oxygen atoms of the framework participate in hydrogen bonding.

The extraordinary feature of cobalt blue **2** and reddish brown **3** is their novel chemical composition and occurrence of one mixed tetrahedral position occupied by Zn/Co and Zn/Fe in the ratio $Zn:T = 0.91:0.09$, where $T = Co, Fe$, respectively. The presence of Co and Fe cations was confirmed by SEM EDX analysis. In **3** a small amount of trivalent iron has been substituted for divalent zinc. It was assumed that the charge balance was accomplished by the simultaneous substitution of H_2en^{2+} cations by electroneutral en.

In order to examine the structural relationships between all known DFT structures (Table 1), a descending Bärnighausen tree has been constructed beginning with an aristotype down to the hettotypes of the lowest monoclinic $C2/c$ symmetry.

A S parameter, that quantifies the degree of lattice distortion and a Δ parameter, which is a measure of similarity of structures, have been used to measure the difference between the structures derived from aristotype, with those of the real structural model. It was observed that the structural differences between ideal and real models vary with cationic radii in tetrahedral positions. A linear dependence was found for the degree of lattice distortion, S , and the measure of similarity, Δ , versus the average ionic radii $(r_T + r_{T'})/2$, where $T = Al, Co, Fe, Ga, Mg, Zn$ and $T' = As, Ge, P$. The structures which incorporate larger tetrahedral cations have higher degree of lattice distortion and are more dissimilar. The $r_T / r_{T'}$ ratio is also reflected in the S , Δ parameters and space group symmetry. The higher values of S and Δ were obtained for the structures with small $r_T / r_{T'}$ ratio, while the structures with significantly larger ratio of ionic radii have middle values of S and Δ . With increasing the $r_T / r_{T'}$ ratio, structures with lower symmetry or apparent disorder were observed.

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References

- [1] J.X. Dong, Y.X. Wang, H. Xu, F. Deng, J. Xu, J.G. Wang, *Micropor. Mesopor. Mater.* 116 (2008) 491-497.
- [2] W.H. Baur, R.X. Fischer, in: W. H. Baur, R. X. Fischer (Eds.), *Zeolite-Type Crystal Structures and their Chemistry*, Springer, Berlin, 2002, pp. 38-52.
- [3] Ch. Baerlocher, L.B. McCusker, D.H. Olson, *Atlas of Zeolite Framework Types*, Sixth revised edition, first impression 2007, Elsevier, Radarweg 29, PO Box 211, 1000 AE Amsterdam, The Netherlands, Linacre House, Jordan Hill, Oxford OX2 8DP, UK, 2007.
- [4] L. Liu, Y. Kong, H. Xu, J.P. Li, J.X. Dong, Z. Lin, *Micropor. Mesopor. Mater.* 115 (2008) 624-628.
- [5] R.H. Jones, J. Chen, G. Sankar, J.M. Thomas, in: J. Weitkamp, H. G. Karge, H. Pfeifer, W. Hoeldrich (Eds.), *Zeolites and Microporous Materials: State of Art*, Elsevier New York, 1994; pp 2229-2236.
- [6] T. Ren, K.E. Christensen, J. Grins, K. Jansson, L. Shi, M. Edén, X. Zou, *Micropor. Mesopor. Mater.* 117 (2009) 285-291.

- [7] S. Neeraj, S. Natarajan, Chem. Mater. 12 (2000) 2753-2762.
- [8] Lj. Karanović, D. Poleti, T. Đorđević, S. Šutović, J. Solid State Chem. 184 (2011) 2506-2515.
- [9] Z. Otwinowski, W. Minor, Methods Enzymol. 276 (1997) 307-326.
- [10] Z. Otwinowski, D. Borek, W. Majewski, W. Minor, Acta Cryst. A59 (2003) 228-234.
- [11] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Cryst. 32 (1999) 115-119.
- [13] L.J. Farrugia, J. Appl. Cryst. 45 (2012) 849-854.
- [14] J.X. Pan, G.Y. Yang, Acta Cryst. E63 (2007) m1925.
- [15] E. Dowty, ATOMS for Windows. Version 5.1. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA, 2000.
- [16] J.V. Smith, Am. Mineral. 63 (1978) 960-969.
- [17] R.D. Shannon, Acta Cryst. A32 (1976) 751-767.
- [18] N.E. Brese, M. O'Keeffe, Acta Cryst. B47 (1991) 192-197.
- [19] F. Capitelli, B. El Bali, R. Essehli, M. Lachkar, V. Valentini, G. Mattei, J. Taraba, Z. Zak, Z. Kristallogr. 221 (2006) 649-655.
- [20] M.G. Giorgini, M.R. Pelletti, G. Paliani, R.S. Catalotti, J. Raman. Spectrosc. 14 (1983) 16-21.
- [21] D. Philip, G. Aruldas, J. Raman Spectrosc. 21 (1990) 211-214.
- [22] H. Bärnighausen, Commun. Math. Chem 9 (1980) 139-175.
- [23] E.S. Tasci, G. de la Flor, D. Orobengoa, C. Capillas, J.M. Perez-Mato, M.I. Aroyo, EPJ Web of Conferences 22 (2012) 00009.
- [24] G. Bergerhoff, M. Berndt, K. Brandenburg, T. Degen, T. Acta Cryst. B55 (1999) 147-156.
- [25] X.H. Bu, P.Y. Feng, T.E. Gier, G.D. Stucky, J. Solid State Chem. 136 (1998) 210-215.

- [26] X.H. Bu, P.Y. Feng, T.E. Gier, G.D. Stucky, J. Am. Chem. Soc. 120 (1998) 13389-13397.
- [27] Y. Ke, G. He, J. Li, Y. Zhang, S. Lu, Z. Lei, Cryst. Res. Technol. 37 (2002) 803-811.
- [28] Y.N. Zhao, J. Jin, Y.U. Kwon, Bull. Korean Chem. Soc. 26 (2005) 1277-1280.
- [29] K.O. Kongshaug, H. Fjellvåg, K.P. Lillerud, Chem. Mater. 12 (2000) 1095-1099.
- [30] J.S. Chen, R.H. Jones, S. Natarajan, M.B. Hursthouse, J.M. Thomas, Angew. Chem. Int. Ed. 33 (1994) 639-640.

Table 1. The chemical formulae, abbreviations, crystal data, and tetrahedral atom density of compounds with DFT framework type.

	Abbreviated Name; Formula; a number of <i>T</i> -cations, <i>Z</i>	Tetrahedral atoms	Space group and unit cell data (Å/ °)	Framework density (No/1000Å ³) ¹	Reference
1	Idealized DFT Framework Type; SiO ₂ <i>T</i> = 8, <i>Z</i> = 8	[Si-Si-O]	<i>P</i> 4 ₂ / <i>mmc</i> (No. 131) <i>a</i> = 7.075, <i>c</i> = 9.023 <i>V</i> = 451.65	17.71	[3]
2	ZCP-DFT ; H ₂ (C ₂ H ₈ N ₂)(Co _{0.3} Zn _{0.7} PO ₄) ₂ <i>T</i> = 32, <i>Z</i> = 8	[Zn-Co-P-O]	<i>P</i> 4 ₂ <i>bc</i> (No. 106) <i>a</i> = 14.7236(6) <i>c</i> = 8.9544(5) <i>V</i> = 1941.17(16)	16.48	[27]
3	DAF-3 ; H ₂ (C ₂ H ₈ N ₂)(ZnPO ₄) ₂ <i>T</i> = 32, <i>Z</i> = 8	[Zn-P-O]	<i>P</i> 4 ₂ <i>bc</i> (No. 106) <i>a</i> = 14.7017* <i>c</i> = 8.9417 <i>V</i> = 1932.66	16.56	[5]
4	UCSB-3GaGe ; H ₂ (C ₂ H ₈ N ₂)(GaGeO ₄) ₂ <i>T</i> = 32, <i>Z</i> = 8	[Ga-Ge-O]	<i>P</i> 4 ₂ / <i>n</i> (No. 86) <i>a</i> = 15.0254(2) <i>c</i> = 8.9822(2) <i>V</i> = 2027.85(6)	15.78	[26]
5	UCSB-3ZnAs, UCSB-3 ; H ₂ (C ₂ H ₈ N ₂)(ZnAsO ₄) ₂ <i>T</i> = 16, <i>Z</i> = 4	[Zn-As-O]	<i>P</i> 4 ₂ / <i>n</i> (No. 86) <i>a</i> = 10.7598(1) <i>c</i> = 9.1015(1) <i>V</i> = 1053.71(2)	15.18	[25]
6	H _{1.8} (C ₂ H ₈ N ₂)(Fe _{0.1} Zn _{0.9} AsO ₄) ₂ <i>T</i> = 16, <i>Z</i> = 4	[Zn-Fe-As-O]	<i>P</i> 4 ₂ / <i>n</i> (No. 86) <i>a</i> = 10.6819(15) <i>c</i> = 9.0590(18) <i>V</i> = 1033.7(3)	15.48	3 -This work
7	H ₂ (C ₂ H ₈ N ₂)(Co _{0.1} Zn _{0.9} AsO ₄) ₂ <i>T</i> = 16, <i>Z</i> = 4	[Zn-Co-As-O]	<i>P</i> 4 ₂ / <i>n</i> (No. 86) <i>a</i> = 10.6845(15) <i>c</i> = 9.0492(18) <i>V</i> = 1033.0(3)	15.49	2 -This work
8	H ₂ (C ₂ H ₈ N ₂)(ZnAsO ₄) ₂ <i>T</i> = 16, <i>Z</i> = 4	[Zn-As-O]	<i>P</i> 4 ₂ / <i>n</i> (No. 86) <i>a</i> = 10.6795(15) <i>c</i> = 9.0528(18) <i>V</i> = 1032.5(3)	15.50	1 -This work
9	UCSB-3GaGe ; H ₂ (C ₂ H ₈ N ₂)(GaGeO ₄) ₂ <i>T</i> = 16, <i>Z</i> = 4	[Ga-Ge-O]	<i>P</i> 4 ₂ / <i>n</i> (No. 86) <i>a</i> = 10.6245(1) <i>c</i> = 8.9822(2) <i>V</i> = 1013.91(3)	15.78	[26]
10	SU-57-I ; H _{1.8} (C ₂ H ₈ N ₂)(Al _{0.90} Ge _{0.73} Si _{0.37} O ₄) ₂	[Al-Ge-Si-O]	<i>P</i> 4 ₂ / <i>n</i> (No. 86) <i>a</i> = 10.4678 (5)	16.36	[6]

	$T = 16, Z = 4$		$c = 8.9227 (6)$ $V = 977.70 (9)$ $P4_2/n$ (No. 86)		
11	ACP-3 ; $H_{1.4}(C_2H_8N_2)(Al_{0.3}Co_{0.7}PO_4)_2$ $T = 16, Z = 4$	[Co-Al-P-O]	$a = 10.4236(1)$ $c = 8.9487(1)$ $V = 972.29(2)$ $P4_2/n$ (No. 86)	16.46	[25]
12	SU-57-II ; $H_{1.88}(C_2H_8N_2)(Al_{0.94}Ge_{0.43}Si_{0.63}O_4)_2$ $T = 16, Z = 4$	[Al-Si-Ge-O]	$a = 10.4464 (6)$ $c = 8.9083 (8)$ $V = 972.14 (12)$ $P4_2/n$ (No. 86)	16.46	[6]
13	$H_2(C_2H_8N_2)(ZnPO_4)_2$ $T = 16, Z = 4$	[Zn-P-O]	$a = 10.3940(8)$ $c = 8.9094(10)$ $V = 962.53(15)$ $P4_2/n$ (No. 86)	16.62	[14]
14	AS-1 ; $H_2(C_2H_8N_2)(AlSiO_4)_2$ $T = 16, Z = 4$	[Al-Si-O]	$a = 10.3022(1)$ $c = 8.8785(1)$ $V = 942.33(2)$ $Pccn$ (No. 56)	16.98	[1]
15	$H_2(C_2H_8N_2)(Fe_{0.4}Zn_{0.6}PO_4)_2$ $T = 16, Z = 4$	[Zn-Fe-P-O]	$a = b = 10.429(3)$ $c = 8.990(3)$ $V = 977.8(5)$ $Pcca$ (No. 54)	16.36	[28]
16	$H_2(C_2H_8N_2)(ZnPO_4)_2$ $T = 32, Z = 8$	[Zn-P-O]	$a = 14.7266(3)$ $b = 8.9439(2)$ $c = 14.6966(3)$ $V = 1935.7(6)$ $C 2/c$ (1)(b) (No. 15)	16.53	4-This work
17	UiO-20 ; $H_2(C_2H_8N_2)(MgPO_4)_2$ $T = 64, Z = 16$	[Mg-P-O]	$a = 20.9098(8)$ $b = 17.8855(7)$ $c = 14.7913(6)$ $\beta = 134.842(2)$ $V = 3922.3 (3)$ $I 2/b$ (3)(c) (No. 15)	16.32	[29]
18	DAF-2 ; $H_2(C_2H_8N_2)(CoPO_4)_2$ $T = 64, Z = 16$	[Co-P-O]	$a = 14.719(6)$ $b = 14.734(5)$ $c = 17.891(6)$ $\gamma = 90.02(2)$ $V = 3880.02^*$	16.49	[30]

*Coordinates and/or standard uncertainties were not given.

[†] The framework density is defined as the number of tetrahedral atoms per 1000 Å³.

Table 2. Crystal data, data collection and refinement details for 1-4.

Crystal data	1	2	3	4
Chemical formula	C ₂ H ₁₀ N ₂ O ₈ As ₂ Zn ₂	C ₂ H ₁₀ N ₂ O ₈ As ₂ Co _{0.2} Zn _{1.8}	C ₂ H _{9.8} N ₂ O ₈ As ₂ Fe _{0.2} Zn _{1.8}	C ₂ H ₁₀ N ₂ O ₈ P ₂ Zn ₂
Temperature (K)	293 (2)	293 (2)	293 (2)	293 (2)
Crystal form, colour	Octahedron-like, colourless	Prismatic, cobalt blue	Prismatic, reddish brown	Prismatic, colourless
Formula weight, M_r (g mol ⁻¹)	470.70	469.57	469.03	382.80
System, space group (No.)	Tetragonal, $P4_2/n$ (86)	Tetragonal, $P4_2/n$ (86)	Tetragonal, $P4_2/n$ (86)	Orthorhombic, $Pcca$ (54)
a (Å)	10.6795 (15)	10.6845 (15)	10.6819 (15)	14.727 (3)
b (Å)	/	/	/	8.9439 (18)
c (Å)	9.0528 (18)	9.0492 (18)	9.0590 (18)	14.697 (3)
V (Å ³)	1032.5 (3)	1033.0 (3)	1033.7 (3)	1935.7 (7)
Z	4	4	4	8
$F(000)$	904	902	901	1520
Calculated density, D_x (g cm ⁻³)	3.028	3.019	3.014	2.627
Absorption coefficient, μ (mm ⁻¹)	11.04	10.91	10.86	5.32
Transmission factors, $T_{\min} / T_{\max}$	0.1857/0.2883	0.5607/0.7356	0.8991/0.8991	0.7769/0.9245
Crystal size (mm)	0.23 × 0.18 × 0.15	0.06 × 0.05 × 0.03	0.10 × 0.07 × 0.03	0.05 × 0.02 × 0.02
Reflections collected/unique	14172/1798	13949/1802	14163/ 1800	19417 / 2615
Observed reflections [$I > 2\sigma(I)$]	1783	1466	1630	2234
R_{int}	0.032	0.099	0.056	0.040
Range for data collection, θ (°)	1.9 – 32.0	1.9 – 32.0	1.9 – 32.0	2.3 – 29.1
Range of Miller indices	$-15 \leq h \leq 15$ $-15 \leq k \leq 15$ $-13 \leq l \leq 13$	$-15 \leq h \leq 15$ $-15 \leq k \leq 15$ $-13 \leq l \leq 13$	$-15 \leq h \leq 15$ $-15 \leq k \leq 15$ $-13 \leq l \leq 13$	$-20 \leq h \leq 20$ $-12 \leq k \leq 12$ $-20 \leq l \leq 20$
Extinction coefficient, k^a	0.0045 (2)	0.0007 (2)	0.0011 (2)	0.0011 (1)
Refined parameters	84	85	85	156
R -indices [$F^2 > 2\sigma(F^2)$] ^b	$R_1 = 0.016$ $wR_2 = 0.039$	$R_1 = 0.033$ $wR_2 = 0.054$	$R_1 = 0.027$ $wR_2 = 0.055$	$R_1 = 0.025$ $wR_2 = 0.071$
R -indices (all data) ^b	$R_1 = 0.016$ $wR_2 = 0.039$	$R_1 = 0.054$ $wR_2 = 0.059$	$R_1 = 0.034$ $wR_2 = 0.057$	$R_1 = 0.032$ $wR_2 = 0.075$

Goodness-of-fit, S	1.19	1.05	1.08	1.11
$(\Delta\rho)_{\max}, (\Delta\rho)_{\min}$ (e Å ⁻³)	0.47, -0.33	0.89, -0.66	0.78, -0.60	0.65, -0.71
^a $F_c^* = F_c k [1 + 0.001 F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$				
^b $w = 1 / [\sigma^2(F_o^2) + (0.0092P)^2 + 1.30P]$ for 1 , $w = 1 / [\sigma^2(F_o^2) + (0.0244P)^2 + 0.00P]$ for 2 , $w = 1 / [\sigma^2(F_o^2) + (0.0259P)^2 + 0.90P]$ for 3 and $w = 1 / [\sigma^2(F_o^2) + (0.0379P)^2 + 2.58P]$ for 4 , where $P = (F_o^2 + 2F_c^2) / 3$				

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters U_{equiv} in 1-4. For the H atoms isotropic U_{iso} is shown.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{equiv}} / U_{\text{iso}}$
1				
Zn12	0.10681 (2)	0.87165 (2)	0.33498 (2)	0.01446 (6)
As11	0.11293 (2)	0.59146 (2)	0.19884 (2)	0.01287 (6)
O11	0.0572 (4)	0.7367 (2)	0.2027 (3)	0.0555 (9)
O12	0.2247 (2)	0.5707 (3)	0.3246 (2)	0.0443 (7)
O2	0.1642 (2)	0.5480 (2)	0.0322 (2)	0.0264 (4)
O3	-0.0003 (3)	0.4956 (3)	0.2577 (2)	0.0463 (7)
N1	-0.1249 (2)	0.6266 (2)	0.4933 (2)	0.0213 (4)
C1 [†]	-0.2230 (5)	0.7114 (5)	0.5571 (5)	0.0198 (9)
C2 [†]	-0.2155 (5)	0.7150 (5)	0.4348 (5)	0.0212 (10)
H1 [†]	-0.0890	0.5835	0.5656	0.032
H2 [†]	-0.0676	0.6725	0.4467	0.032
H3 [†]	-0.1605	0.5741	0.4295	0.032
H4 [†]	-0.0880	0.5864	0.4188	0.032
H5 [†]	-0.1638	0.5718	0.5511	0.032
H6 [†]	-0.0675	0.6679	0.5451	0.032
H11 [†]	-0.1851	0.7682	0.6272	0.024
H12 [†]	-0.2856	0.6619	0.6082	0.024
H21 [†]	-0.2794	0.6701	0.3791	0.025
H22 [†]	-0.1743	0.7724	0.3671	0.025
2				
Tl2 [*]	0.10702 (4)	0.87188 (4)	0.33512 (4)	0.01894 (14)
As11	0.11281 (3)	0.59176 (3)	0.19889 (3)	0.01766 (11)
O11	0.0574 (4)	0.7362 (3)	0.2023 (3)	0.0575 (12)
O12	0.2241 (3)	0.5717 (4)	0.3253 (3)	0.0487 (10)
O2	0.1646 (3)	0.5480 (3)	0.0322 (3)	0.0306 (7)
O3	-0.0001 (4)	0.4957 (4)	0.2570 (3)	0.0472 (10)
N1	-0.1245 (3)	0.6266 (3)	0.4934 (4)	0.0251 (7)
C1 [†]	-0.2147 (8)	0.7160 (8)	0.4342 (11)	0.027 (2)
C2 [†]	-0.2233 (8)	0.7132 (8)	0.5578 (11)	0.024 (2)

H1 [!]	-0.0874	0.5846	0.5661	0.038
H2 [!]	-0.0684	0.6718	0.4449	0.038
H3 [!]	-0.1611	0.5729	0.4319	0.038
H4 [!]	-0.0878	0.5846	0.4198	0.038
H5 [!]	-0.1632	0.5728	0.5527	0.038
H6 [!]	-0.0659	0.6675	0.5445	0.038
H11 [!]	-0.2782	0.6723	0.3757	0.032
H12 [!]	-0.1730	0.7751	0.3678	0.032
H21 [!]	-0.2852	0.6640	0.6117	0.029
H22 [!]	-0.1845	0.7706	0.6272	0.029
Occ. (Zn)	0.914 (14)			
Occ. (Co)	0.086 (14)			
3				
Tl2**	0.10697 (3)	0.87180 (4)	0.33497 (3)	0.01850 (11)
As11	0.11281 (3)	0.59158 (3)	0.19897 (3)	0.01691 (9)
O11	0.0574 (4)	0.7362 (3)	0.2033 (3)	0.0593 (11)
O12	0.2246 (3)	0.5718 (4)	0.3250 (3)	0.0475 (9)
O2	0.1640 (3)	0.5480 (3)	0.0322 (3)	0.0308 (6)
O3	0.0005 (3)	0.4951 (3)	0.2576 (3)	0.0482 (9)
N1	-0.1249 (3)	0.6265 (3)	0.4941 (3)	0.0258 (6)
C1 [!]	-0.2232 (6)	0.7116 (7)	0.5580 (7)	0.0218 (14)
C2 [!]	-0.2157 (7)	0.7160 (7)	0.4358 (8)	0.0251 (15)
H1 [!]	-0.0874	0.5846	0.5661	0.039
H2 [!]	-0.0684	0.6718	0.4449	0.039
H3 [!]	-0.1611	0.5729	0.4319	0.039
H4 [!]	-0.0878	0.5846	0.4198	0.039
H5 [!]	-0.1632	0.5728	0.5527	0.039
H6 [!]	-0.0659	0.6675	0.5445	0.039
H11 [!]	-0.2852	0.6640	0.6117	0.026
H12 [!]	-0.1845	0.7706	0.6272	0.026
H21 [!]	-0.2782	0.6723	0.3757	0.030
H22 [!]	-0.1730	0.7751	0.3678	0.030
Occ. (Zn)	0.909 (10)			
Occ. (Fe)	0.091 (10)			
4				

Zn11	0.13146 (2)	0.34264 (3)	-0.25779 (2)	0.01292 (10)
Zn12	-0.01042 (2)	0.15691 (3)	0.11828 (2)	0.01484 (10)
P13	0.14636 (4)	0.29800 (7)	0.23889 (4)	0.01001 (13)
P14	0.01141 (4)	0.20093 (7)	-0.10234 (4)	0.01062 (13)
O11	0.10380 (18)	0.2854 (3)	0.33217 (15)	0.0387 (6)
O12	0.10590 (14)	0.1822 (2)	0.17380 (15)	0.0258 (5)
O13	-0.07834 (13)	0.2079 (2)	-0.15337 (14)	0.0247 (4)
O14	0.07950 (15)	0.3175 (2)	-0.13849 (14)	0.0251 (5)
O21	0.13491 (13)	0.5460 (2)	-0.30171 (13)	0.0205 (4)
O22	-0.05383 (12)	-0.04614 (19)	0.10795 (13)	0.0175 (4)
O31	0.24692 (13)	0.2572 (3)	0.24723 (17)	0.0325 (6)
O32	-0.00597 (12)	0.2459 (2)	-0.00279 (13)	0.0183 (4)
N1	0.12286 (15)	0.5114 (2)	0.00588 (15)	0.0174 (4)
N21	0.2500	0.0	0.6239 (2)	0.0190 (6)
N22	0.2500	0.0	0.3680 (2)	0.0285 (8)
C1	0.21714 (17)	0.5656 (3)	0.0006 (2)	0.0185 (5)
C21 [†]	0.2505 (4)	0.0596 (6)	0.5303 (4)	0.0192 (10)
C22 [†]	0.2550 (3)	-0.0676 (6)	0.4622 (4)	0.0166 (9)
H11	0.0850	0.5890	0.0059	0.026
H12	0.1154	0.4591	0.0568	0.026
H13	0.1111	0.4534	-0.0419	0.026
H211 [†]	0.2473	0.0754	0.6633	0.028
H212 [†]	0.3005	-0.0523	0.6335	0.028
H213 [†]	0.2019	-0.0590	0.6313	0.028
H221 [†]	0.2525	-0.0724	0.3266	0.043
H222 [†]	0.2965	0.0622	0.3601	0.043
H223 [†]	0.1981	0.0500	0.3620	0.043
H14	0.2298	0.6300	0.0522	0.022
H15	0.2252	0.6237	-0.0545	0.022
H214 [†]	0.3025	0.1248	0.5221	0.023
H215 [†]	0.1960	0.1179	0.5199	0.023
H224 [†]	0.3112	-0.1227	0.4695	0.020
H225 [†]	0.2047	-0.1359	0.4716	0.020

* $T12 = \text{Zn}_{0.9}\text{Co}_{0.1}$; ** $T12 = \text{Zn}_{0.9}\text{Fe}_{0.1}$; [†] Atoms located in general position with site occupation factors equal to 0.5.

Table 4. Anisotropic displacement parameters ($\text{\AA}^2$) for 1-4.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
1						
Zn12	0.01349 (12)	0.01498 (12)	0.01489 (10)	0.00236 (10)	0.00108 (8)	0.00036 (8)
As11	0.01152 (10)	0.01308 (10)	0.01401 (8)	-0.00213 (8)	-0.00031 (7)	-0.00216 (7)
O11	0.105 (3)	0.0229 (11)	0.0385 (12)	0.0266 (13)	-0.0257 (15)	-0.0186 (10)
O12	0.0164 (9)	0.093 (2)	0.0238 (10)	-0.0149 (10)	-0.0073 (7)	0.0246 (12)
O2	0.0319 (10)	0.0344 (11)	0.0131 (7)	0.0168 (8)	0.0058 (7)	0.0059 (7)
O3	0.0455 (15)	0.0721 (18)	0.0211 (8)	-0.0488 (13)	0.0033 (10)	-0.0059 (12)
N1	0.0227 (9)	0.0207 (9)	0.0204 (8)	0.0015 (8)	0.0031 (8)	0.0004 (7)
C1	0.018 (2)	0.027 (2)	0.015 (2)	0.0072 (16)	0.0001 (16)	-0.0002 (18)
C2	0.024 (2)	0.025 (2)	0.014 (2)	0.0036 (18)	-0.0016 (17)	-0.0006 (17)
2						
*Tl2	0.0181 (2)	0.0194 (2)	0.0193 (2)	0.00278 (19)	0.00133 (16)	0.00050 (17)
As11	0.0166 (2)	0.0178 (2)	0.01856 (17)	-0.00261 (16)	-0.00021 (14)	-0.00232 (14)
O11	0.103 (3)	0.0286 (18)	0.041 (2)	0.0286 (19)	-0.021 (2)	-0.0166 (16)
O12	0.0225 (16)	0.094 (3)	0.0295 (19)	-0.0118 (17)	-0.0062 (13)	0.0276 (19)
O2	0.0342 (18)	0.0400 (18)	0.0175 (16)	0.0154 (13)	0.0052 (12)	0.0048 (13)
O3	0.047 (2)	0.068 (3)	0.0266 (15)	-0.0425 (18)	0.0047 (16)	-0.0026 (18)
N1	0.0262 (17)	0.0252 (16)	0.0237 (15)	0.0006 (14)	0.0015 (15)	0.0023 (13)
C1	0.027 (5)	0.030 (5)	0.023 (6)	0.004 (3)	-0.007 (4)	0.001 (4)
C2	0.019 (5)	0.032 (5)	0.022 (6)	0.003 (3)	-0.001 (3)	-0.001 (4)
3						
**Tl2	0.01745 (19)	0.01907 (19)	0.01897 (17)	0.00261 (14)	0.00100 (13)	0.00052 (14)
As11	0.01556 (16)	0.01698 (16)	0.01820 (14)	-0.00227 (12)	-0.00037 (11)	-0.00219 (11)
O11	0.111 (3)	0.0262 (15)	0.0406 (17)	0.0294 (17)	-0.0249 (19)	-0.0195 (13)
O12	0.0241 (14)	0.091 (3)	0.0275 (14)	-0.0151 (15)	-0.0078 (11)	0.0214 (16)
O2	0.0351 (15)	0.0384 (15)	0.0191 (12)	0.0167 (11)	0.0050 (10)	0.0036 (10)
O3	0.048 (2)	0.071 (2)	0.0261 (12)	-0.0449 (17)	0.0048 (14)	-0.0065 (16)
N1	0.0256 (14)	0.0254 (13)	0.0263 (12)	0.0025 (11)	0.0037 (12)	0.0008 (11)
C1	0.017 (3)	0.031 (4)	0.017 (3)	0.007 (2)	0.001 (2)	0.001 (3)
C2	0.026 (4)	0.024 (4)	0.025 (4)	0.002 (2)	-0.001 (3)	-0.001 (3)
4						

Zn11	0.01207 (15)	0.01316 (16)	0.01352 (16)	-0.00042 (10)	0.00089 (10)	0.00004 (10)
Zn12	0.01748 (16)	0.01380 (16)	0.01322 (16)	-0.00029 (10)	-0.00052 (11)	-0.00055 (10)
P13	0.0087 (3)	0.0102 (3)	0.0111 (3)	-0.0014 (2)	0.0001 (2)	-0.0004 (2)
P14	0.0134 (3)	0.0090 (3)	0.0095 (3)	0.0003 (2)	0.0013 (2)	0.0013 (2)
O11	0.0612 (15)	0.0296 (12)	0.0253 (11)	-0.0225 (11)	0.0269 (11)	-0.0051 (9)
O12	0.0276 (10)	0.0170 (10)	0.0329 (12)	0.0033 (8)	-0.0162 (9)	-0.0099 (8)
O13	0.0258 (10)	0.0231 (10)	0.0254 (10)	0.0059 (8)	-0.0113 (9)	0.0043 (8)
O14	0.0397 (12)	0.0173 (10)	0.0184 (9)	-0.0123 (8)	0.0157 (9)	-0.0045 (7)
O21	0.0295 (10)	0.0115 (8)	0.0207 (10)	-0.0036 (7)	-0.0039 (8)	-0.0010 (7)
O22	0.0136 (8)	0.0111 (8)	0.0279 (10)	0.0011 (6)	-0.0012 (7)	-0.0017 (7)
O31	0.0073 (8)	0.0205 (10)	0.0696 (18)	-0.0022 (7)	-0.0037 (9)	0.0098 (10)
O32	0.0260 (9)	0.0188 (9)	0.0101 (8)	0.0019 (7)	0.0052 (7)	0.0019 (7)
N1	0.0148 (10)	0.0163 (10)	0.0212 (11)	0.0011 (8)	-0.0010 (8)	-0.0018 (9)
N21	0.0242 (16)	0.0166 (15)	0.0161 (15)	-0.0046 (12)	0.0	0.0
N22	0.038 (2)	0.033 (2)	0.0155 (16)	-0.0014 (16)	0.0	0.0
C1	0.0161 (11)	0.0109 (11)	0.0286 (14)	-0.0009 (9)	0.0002 (10)	0.0014 (10)
C21	0.026 (3)	0.016 (2)	0.016 (3)	0.001 (2)	0.002 (2)	0.0031 (19)
C22	0.015 (2)	0.014 (2)	0.021 (3)	-0.0016 (17)	-0.001 (2)	0.000 (2)

*T12 = Zn_{0.9}Co_{0.1}; **T12 = Zn_{0.9}Fe_{0.1}

Table 5. Selected bond distances (Å) and bond angles (°) in 1-4.

1					
Zn12—O12 ⁱ	1.905(2)	N1—C2	1.452(6)	O11—As11—O12	111.52(16)
Zn12—O2 ⁱⁱ	1.9305(17)	N1—C1	1.501(6)	O11—As11—O2	113.30(11)
Zn12—O3 ⁱⁱⁱ	1.9414(17)	C1—C2 ^{vi}	1.507(6)	O12—As11—O2	110.25(11)
Zn12—O11	1.947(2)			O11—As11—O3	107.8(2)
<Zn12—O> [!]	1.9310(47)	O12 ⁱ —Zn12—O2 ⁱⁱ	114.64(9)	O12—As11—O3	102.65(12)
As11—O11	1.662(2)	O12 ⁱ —Zn12—O3 ⁱⁱⁱ	106.45(16)	O2—As11—O3	110.77(11)
As11—O12	1.6643(19)	O2 ⁱⁱ —Zn12—O3 ⁱⁱⁱ	110.85(10)	N1—C2—C1 ^{vi}	111.2(3)
As11—O2	1.6708(17)	O12 ⁱ —Zn12—O11	117.80(14)	N1—C1—C2 ^{vi}	109.6(3)
As11—O3	1.6717(17)	O2 ⁱⁱ —Zn12—O11	109.48(11)		
<As11—O> ^{!a}	1.6672(12)	O3 ⁱⁱⁱ —Zn12—O11	95.88(11)	N1—C1—C2 ^{vi} —N1 ^{vi}	-176.7
Symmetry codes: (i) -x+1/2, -y+3/2, z; (ii) y-1/2, -x+1, z+1/2; (iii) -y+1/2, x+1, -z+1/2; (iv) -y+1, x+1/2, z-1/2; (v) y-1, -x+1/2, -z+1/2; (vi) -x-1/2, -y+3/2, z.					
2					
[*] T12—O12 ⁱ	1.904 (3)	N1—C2	1.462 (9)	O11—As11—O12	111.3 (2)
T12—O2 ⁱⁱ	1.932 (3)	N1—C1	1.517 (10)	O11—As11—O3	108.0 (3)
T12—O3 ⁱⁱⁱ	1.942 (3)	C1—C2 ^{vi}	1.503 (10)	O12—As11—O3	102.76 (17)
T12—O11	1.957 (3)			O11—As11—O2	113.32 (16)
<T12—O> [!]	1.9335(55)	O12 ⁱ —T 12—O2 ⁱⁱ	114.61 (13)	O12—As11—O2	110.30 (16)
As11—O11	1.653 (3)	O12 ⁱ —T 12—O3 ⁱⁱⁱ	107.0 (2)	O3—As11—O2	110.56 (17)
As11—O12	1.664 (3)	O2 ⁱⁱ —T 12—O3 ⁱⁱⁱ	110.75 (14)	N1—C2—C1 ^{vi}	109.3 (3)
As11—O3	1.669 (2)	O12 ⁱ —T 12—O11	117.55 (18)	N1—C1—C2 ^{vi}	110.3 (6)
As11—O2	1.673 (3)	O2 ⁱⁱ —T 12—O11	109.23 (15)		
<As11—O> ^{!a}	1.6648(22)	O3 ⁱⁱⁱ —T 12—O11	96.02 (16)	N1—C1—C2 ^{vi} —N1 ^{vi}	-176.6
Symmetry codes: (i) -x+1/2, -y+3/2, z; (ii) y-1/2, -x+1, z+1/2; (iii) -y+1/2, x+1, -z+1/2; (iv) -y+1, x+1/2, z-1/2; (v) y-1, -x+1/2, -z+1/2; (vi) -x-1/2, -y+3/2, z.					
3					
^{**} T12—O12 ⁱ	1.900 (3)	N1—C2	1.461 (8)	O11—As11—O12	111.03 (19)
T12—O2 ⁱⁱ	1.933 (2)	N1—C1	1.505 (7)	O11—As11—O3	108.2 (2)
T12—O3 ⁱⁱⁱ	1.945 (2)	C1—C2 ^{vi}	1.499 (8)	O12—As11—O3	102.66 (15)
T12—O11	1.950 (3)			O11—As11—O2	113.48 (14)
<T12—O> [!]	1.932 (11)	O12 ⁱ —T 12—O2 ⁱⁱ	114.56 (12)	O12—As11—O2	110.44 (14)
As11—O11	1.655 (3)	O12 ⁱ —T 12—O3 ⁱⁱⁱ	106.65 (19)	O3—As11—O2	110.52 (15)
As11—O12	1.665 (3)	O2 ⁱⁱ —T 12—O3 ⁱⁱⁱ	110.83 (13)	N1—C2—C1 ^{vi}	111.1 (6)
As11—O3	1.668 (2)	O12 ⁱ —T 12—O11	117.64 (17)	N1—C1—C2 ^{vi}	109.1 (6)
As11—O2	1.673 (2)	O2 ⁱⁱ —T 12—O11	109.27 (14)		
<As11—O> ^{!a}	1.665 (4)	O3 ⁱⁱⁱ —T 12—O11	96.25 (14)	N1—C1—C2 ^{vi} —N1 ^{vi}	-176.5
Symmetry codes: (i) -x+1/2, -y+3/2, z; (ii) y-1/2, -x+1, z+1/2; (iii) -y+1/2, x+1, -z+1/2; (iv) -y+1, x+1/2, z-1/2; (v) y-1, -x+1/2, -z+1/2; (vi) -x-1/2, -y+3/2, z.					

4					
Zn11—O14	1.9261(19)	N1—C1	1.473 (3)	O11—P13—O21 ^{iv}	112.14 (13)
Zn11—O21	1.9309(18)	N21—C21	1.475 (6)	O11—P13—O31	108.11 (15)
Zn11—O13 ⁱ	1.9416(19)	N22—C22	1.512 (6)	O21 ^{iv} —P13—O31	110.87 (12)
Zn11—O31 ⁱⁱ	1.949 (2)	C1—C1 ^{viii}	1.521 (5)	O11—P13—O12	110.79 (13)
<Zn11—O> ^{!a}	1.9369(26)	C21—C22	1.516 (8)	O21 ^{iv} —P13—O12	109.33 (11)
Zn12—O12	1.9109(19)			O31—P13—O12	105.40 (12)
Zn12—O22	1.9313(18)			O13—P14—O22 ^v	111.55 (11)
Zn12—O11 ⁱⁱⁱ	1.934 (2)	O14—Zn11—O21	115.13 (8)	O13—P14—O32	108.28 (11)
Zn12—O32	1.951 (2)	O14—Zn11—O13 ⁱ	112.31 (9)	O22 ^v —P14—O32	110.97 (11)
<Zn12—O> ^{!a}	1.9318(41)	O21—Zn11—O13 ⁱ	111.76 (8)	O13—P14—O14	111.58 (12)
P13—O11	1.512 (2)	O14—Zn11—O31 ⁱⁱ	106.56 (10)	O22 ^v —P14—O14	109.27 (11)
P13—O21 ^{iv}	1.5265(19)	O21—Zn11—O31 ⁱⁱ	110.97 (9)	O32—P14—O14	105.01 (11)
P13—O31	1.530 (2)	O13 ⁱ —Zn11—O31 ⁱⁱ	98.76 (10)	N1—C1—C1 ^{viii}	110.3 (3)
P13—O12	1.530 (2)	O12—Zn12—O22	116.22 (8)	N21—C21—C22	110.1 (4)
<P13—O> [!]	1.5246(21)	O12—Zn12—O11 ⁱⁱⁱ	113.96 (10)	N22—C22—C21	107.6 (4)
P14—O13	1.521 (2)	O22—Zn12—O11 ⁱⁱⁱ	110.67 (10)		
P14—O22 ^v	1.5211(18)	O12—Zn12—O32	108.12 (9)		
P14—O32	1.539 (2)	O22—Zn12—O32	108.86 (9)	N1—C1—C1 ^{viii} —N1 ^{viii}	-173.6
P14—O14	1.541 (2)	O11 ⁱⁱⁱ —Zn12—O32	97.17 (9)	N21—C21—C22—N22	176.9
<P14—O> [!]	1.5305(27)				

Symmetry codes: (i) -x, y, -z-1/2; (ii) -x+1/2, y, z-1/2; (iii) -x, y, -z+1/2; (iv) x, -y+1, z+1/2;
(v) -x, -y, -z; (vi) x, -y+1, z-1/2; (vii) -x+1/2, y, z+1/2; (viii) -x+1/2, -y+1, z.

*T12 = Zn_{0.9}Co_{0.1}; **T12 = Zn_{0.9}Fe_{0.1}; [!] Calculated as $\sigma_d = \sqrt{\sum_m (d_m - \bar{d})^2 / m(m-1)}$

Table 6. Hydrogen bond geometry (Å, °) in 1-4.

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	∠ <i>D</i> –H... <i>A</i>	<i>D</i> ... <i>A</i>
1				
N1–H1...O3 ^{vii}	0.89	2.041	173.16	2.928
N1–H2...O2 ⁱⁱ	0.89	2.275	129.23	2.920
N1–H3...O11 ^v	0.89	2.146	173.09	3.030
N1–H4...O3	0.89	1.988	176.08	2.877
N1–H5...O12 ^{vii}	0.89	2.003	168.80	2.880
N1–H6...O2 ⁱⁱ	0.89	2.169	141.86	2.920
Symmetry codes: (i) -x+1/2, -y+3/2, z; (ii) y-1/2, -x+1, z+1/2; (iii) -y+1/2, x+1, -z+1/2; (iv) -y+1, x+1/2, z-1/2; (v) y-1, -x+1/2, -z+1/2; (vi) -x-1/2, -y+3/2, z; (vii) -x, -y+1, -z+1.				
2				
N1–H1...O3 ^{vii}	0.89	2.044	173.18	2.930
N1–H2...O2 ⁱⁱ	0.89	2.273	129.09	2.914
N1–H3...O11 ^v	0.89	2.150	173.27	3.036
N1–H4...O3	0.89	1.992	176.36	2.880
N1–H5...O12 ^{vii}	0.89	2.008	168.15	2.885
N1–H6...O2 ⁱⁱ	0.89	2.165	141.28	2.914
Symmetry codes: (i) -x+1/2, -y+3/2, z; (ii) y-1/2, -x+1, z+1/2; (iii) -y+1/2, x+1, -z+1/2; (iv) -y+1, x+1/2, z-1/2; (v) y-1, -x+1/2, -z+1/2; (vi) -x-1/2, -y+3/2, z; (vii) -x, -y+1, -z+1.				
3				
N1–H1...O3 ^{vii}	0.89	2.042	174.47	2.929
N1–H2...O2 ⁱⁱ	0.89	2.286	127.81	2.915
N1–H3...O11 ^v	0.89	2.148	174.67	3.036
N1–H4...O3	0.89	1.988	177.68	2.881
N1–H5...O12 ^{vii}	0.89	2.006	168.86	2.884
N1–H6...O2 ⁱⁱ	0.89	2.170	140.48	2.915
Symmetry codes: (i) -x+1/2, -y+3/2, z; (ii) y-1/2, -x+1, z+1/2; (iii) -y+1/2, x+1, -z+1/2; (iv) -y+1, x+1/2, z-1/2; (v) y-1, -x+1/2, -z+1/2; (vi) -x-1/2, -y+3/2, z; (vii) -x, -y+1, -z+1.				
4				

N1–H11...O32 ^{ix}	0.89	1.879	178.61	2.769
N1–H12...O21 ^{iv}	0.89	2.098	146.00	2.880
N1–H13...O14	0.89	1.926	175.24	2.814
N21–H211...O31 ^{vii}	0.89	2.043	173.93	2.929
N21–H212...O13 ^x	0.89	2.281	174.04	3.168
N21–H213...O12 ^{xi}	0.89	1.898	167.83	2.775
N22–H221...O31 ^{xii}	0.89	2.023	171.70	2.906
N22–H222...O22 ^x	0.89	2.259	133.10	2.939
N22–H223...O22 ⁱⁱⁱ	0.89	2.334	125.32	2.939
N22–H223...O11	0.89	2.560	153.64	3.381

Symmetry codes: (i) $-x, y, -z-1/2$; (ii) $-x+1/2, y, z-1/2$; (iii) $-x, y, -z+1/2$; (iv) $x, -y+1, z+1/2$; (v) $-x, -y, -z$; (vi) $x, -y+1, z-1/2$; (vii) $-x+1/2, y, z+1/2$; (viii) $-x+1/2, -y+1, z$; (ix) $-x, -y+1, -z$; (x) $x+1/2, -y, -z+1/2$; (xi) $x, -y, z+1/2$; (xii) $-x+1/2, -y, z$.

Table 7. Bond-valences v_{ij} (valence units) for 1-4.

1					
	Zn12	As11	Σv_{ij}		
O11	0.519	1.328	1.847		
O12	0.581	1.321	1.902		
O2	0.541	1.296	1.837		
O3	0.527	1.293	1.820		
Σv_{ij}	2.168	5.238			
2					
	$T12^*$	As11	Σv_{ij}		
O11	0.503	1.361	1.864		
O12	0.580	1.321	1.901		
O2	0.538	1.289	1.827		
O3	0.524	1.303	1.827		
Σv_{ij}	2.145	5.274			
3					
	$T12^{**}$	As11	Σv_{ij}		
O11	0.522	1.354	1.876		
O12	0.598	1.317	1.915		
O2	0.548	1.289	1.837		
O3	0.529	1.307	1.836		
Σv_{ij}	2.197	5.267			
4					
	Zn11	Zn12	P13	P14	$\Sigma v_{ij}^{\dagger}$
O11	—	0.537	1.328	—	1.865
O12	—	0.572	1.265	—	1.837
O13	0.526	—	—	1.296	1.822
O14	0.549	—	—	1.228	1.777
O21	0.541	—	1.279	—	1.820
O22	—	0.541	—	1.296	1.837
O31	0.516	—	1.265	—	1.781
O32	—	0.513	—	1.235	1.748
Σv_{ij}	2.132	2.163	5.137	5.055	

^{*}*T12* = Zn_{0.9}Co_{0.1}; ^{**}*T12* = Zn_{0.9}Fe_{0.1};

[†] The contribution from the hydrogen bonds were neglect.

Table 8. The atomic site relationship of the DFT-zeotype crystal structures and the initial estimate for the unit cell parameters.

Aristotype <i>P4₂/mmc</i> (No.131)	<i>P4₂bc</i> (No.106)	<i>P4₂/n</i> (No. 86)	<i>Pccn</i> (No. 56)	<i>Pcca</i> (No. 54)	<i>C 2/c</i> (1)(b) (No. 15)	<i>I 2/b</i> (3)(c) (No. 15)
<i>T</i> (8p) [.m.]	<i>T</i> 11(8c) [1] <i>T</i> 12(8c) [1] <i>T</i> 13(8c) [1] <i>T</i> 14(8c) [1]	<i>T</i> 11(8g) [1] <i>T</i> 12(8g) [1]	<i>T</i> 11(8e) [1] <i>T</i> 12(8e) [1]	<i>T</i> 11(8c) [1] <i>T</i> 12(8c) [1] <i>T</i> 13(8c) [1] <i>T</i> 14(8c) [1]	<i>T</i> 11(8f) [1] <i>T</i> 12(8f) [1] <i>T</i> 13(8f) [1] <i>T</i> 14(8f) [1] <i>T</i> 15(8f) [1] <i>T</i> 16(8f) [1] <i>T</i> 17(8f) [1] <i>T</i> 18(8f) [1]	<i>T</i> 11(8f) [1] <i>T</i> 12(8f) [1] <i>T</i> 13(8f) [1] <i>T</i> 14(8f) [1] <i>T</i> 15(8f) [1] <i>T</i> 16(8f) [1] <i>T</i> 17(8f) [1] <i>T</i> 18(8f) [1]
<i>O</i> 1(8n) [...2]	<i>O</i> 11(8c) [1] <i>O</i> 12(8c) [1] <i>O</i> 13(8c) [1] <i>O</i> 14(8c) [1]	<i>O</i> 11(8g) [1] <i>O</i> 12(8g) [1]	<i>O</i> 11(8e) [1] <i>O</i> 12(8e) [1]	<i>O</i> 11(8c) [1] <i>O</i> 12(8c) [1] <i>O</i> 13(8c) [1] <i>O</i> 14(8c) [1]	<i>O</i> 11(8f) [1] <i>O</i> 12(8f) [1] <i>O</i> 13(8f) [1] <i>O</i> 14(8f) [1] <i>O</i> 15(8f) [1] <i>O</i> 16(8f) [1] <i>O</i> 17(8f) [1] <i>O</i> 18(8f) [1]	<i>O</i> 11(8f) [1] <i>O</i> 12(8f) [1] <i>O</i> 13(8f) [1] <i>O</i> 14(8f) [1] <i>O</i> 15(8f) [1] <i>O</i> 16(8f) [1] <i>O</i> 17(8f) [1] <i>O</i> 18(8f) [1]
<i>O</i> 2(4m) [m2m.]	<i>O</i> 21(8c) [1] <i>O</i> 22(8c) [1]	<i>O</i> 2(8g) [1]	<i>O</i> 2(8e) [1]	<i>O</i> 21(8c) [1] <i>O</i> 22(8c) [1]	<i>O</i> 21(8f) [1] <i>O</i> 22(8f) [1] <i>O</i> 23(8f) [1] <i>O</i> 24(8f) [1]	<i>O</i> 21(8f) [1] <i>O</i> 22(8f) [1] <i>O</i> 23(8f) [1] <i>O</i> 24(8f) [1]
<i>O</i> 3(4i) [2mm.]	<i>O</i> 31(8c) [1] <i>O</i> 32(8c) [1]	<i>O</i> 3(8g) [1]	<i>O</i> 3(8e) [1]	<i>O</i> 31(8c) [1] <i>O</i> 32(8c) [1]	<i>O</i> 31(8f) [1] <i>O</i> 32(8f) [1] <i>O</i> 33(8f) [1] <i>O</i> 34(8f) [1]	<i>O</i> 31(8f) [1] <i>O</i> 32(8f) [1] <i>O</i> 33(8f) [1] <i>O</i> 34(8f) [1]
$a = 7.075 \text{ \AA}$ $c = 9.023 \text{ \AA}$ $V = 451.65 \text{ \AA}^3$	$a' \approx 2a$ $b' \approx 2a$ $c' \approx c$ $V' \approx 4V$	$a' \approx a-b$ $b' \approx a+b$ $c' \approx c$ $V' \approx 2V$	$a' \approx a-b$ $b' \approx a+b$ $c' \approx c$ $V' \approx 2V$	$a' \approx 2a$ $b' \approx c$ $c' \approx 2a$ $V' \approx 4V$	$a' \approx 2a-2b$ $b' \approx 2c$ $c' \approx 2a$ $\beta \approx 135$ $V' \approx 8V$	$a' \approx 2a$ $b' \approx 2a$ $c' \approx 2c$ $\gamma \approx 90$ $V' \approx 8V$

Table 9. The degree of lattice distortion and the structure similarity of the DFT-zeotype crystal structures.

Abbreviated Name; Formula; A number of T-cations, Z, Space Group	Legend	S	$d_{\max.}(\text{\AA})$	$d_{\text{av.}}(\text{\AA})$	Δ	References
ZCP-DFT; $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{Co}_{0.3}\text{Zn}_{0.7}\text{PO}_4)_2$ T = 32, Z= 8, $\text{P4}_2/\text{bc}$ (No. 106)	ZnCoP-106	0.0197	0.9746	0.2957	0.096	[27]
UCSB-3ZnAs, UCSB-3; $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{ZnAsO}_4)_2$ T = 16, Z= 4, $\text{P4}_2/\text{n}$ (No. 86_2)	ZnAs-86	0.0370	1.0441	0.4785	0.127	[25]
$\text{H}_{1.8}(\text{C}_2\text{H}_8\text{N}_2)(\text{Fe}_{0.1}\text{Zn}_{0.9}\text{AsO}_4)_2$ T = 16, Z= 4, $\text{P4}_2/\text{n}$ (No. 86_2)	3-ZnFeAs-86	0.0330	1.0361	0.4746	0.124	3 – this work
$\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{Co}_{0.1}\text{Zn}_{0.9}\text{AsO}_4)_2$ T = 16, Z= 4, $\text{P4}_2/\text{n}$ (No. 86_2)	2-ZnCoAs-86	0.0331	1.0390	0.4757	0.126	2 – this work
$\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{ZnAsO}_4)_2$ T = 16, Z= 4, $\text{P4}_2/\text{n}$ (No. 86_2)	1-ZnAs-86	0.0328	1.0359	0.4743	0.124	1 – this work
UCSB-3GaGe; $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{GaGeO}_4)_2$ T = 16, Z= 4, $\text{P4}_2/\text{n}$ (No. 86_2)	GaGe-86	0.0301	0.9642	0.4271	0.122	[26]
SU-57-I; $\text{H}_{1.8}(\text{C}_2\text{H}_8\text{N}_2)(\text{Al}_{0.90}\text{Ge}_{0.73}\text{Si}_{0.37}\text{O}_4)_2$ T = 16, Z= 4, $\text{P4}_2/\text{n}$ (No. 86_2)	AlGe-86	0.0226	0.7913	0.2897	0.103	[6]
ACP-3; $\text{H}_{1.4}(\text{C}_2\text{H}_8\text{N}_2)(\text{Al}_{0.3}\text{Co}_{0.7}\text{PO}_4)_2$ T = 16, Z= 4, $\text{P4}_2/\text{n}$ (No. 86_2)	CoAlP-86	0.0203	0.9097	0.4274	0.106	[25]
SU-57-II; $\text{H}_{1.88}(\text{C}_2\text{H}_8\text{N}_2)(\text{Al}_{0.94}\text{Ge}_{0.43}\text{Si}_{0.63}\text{O}_4)_2$ T = 16, Z= 4, $\text{P4}_2/\text{n}$ (No. 86_2)	AlSiGe-86	0.0226	0.7857	0.2844	0.102	[6]
$\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{ZnPO}_4)_2$ T = 16, Z= 4, $\text{P4}_2/\text{n}$ (No. 86_2)	ZnP-86	0.0191	0.9134	0.4227	0.107	[14]
AS-1; $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{AlSiO}_4)_2$ T = 16, Z= 4, $\text{P4}_2/\text{n}$ (No. 86_2)	AlSi-86	0.0151	0.6163	0.2831	0.085	[1]
$\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{Fe}_{0.4}\text{Zn}_{0.6}\text{PO}_4)_2$ T = 16, Z= 4, Pccn (No. 56)	FeZnPI-56*	0.0204	0.9554	0.4272	0.100	[28]
$\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{Fe}_{0.4}\text{Zn}_{0.6}\text{PO}_4)_2$ T = 16, Z= 4, Pccn (No. 56)	FeZnPII-56**	0.0204	0.9573	0.4281	0.100	[28]
$\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{ZnPO}_4)_2$ T = 32, Z= 8, Pcca (No. 54)	4-ZnP-54	0.0193	0.9909	0.3077	0.105	4 – this work
UiO-20; $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{MgPO}_4)_2$ T = 64, Z= 16, C2/c (No. 15)	MgP-15	0.0227	0.9478	0.1745	0.098	[29]
DAF-2; $\text{H}_2(\text{C}_2\text{H}_8\text{N}_2)(\text{CoPO}_4)_2$ T = 64, Z= 16, C2/c (No. 15)	CoP-15	0.0227	0.9866	0.1804	0.097	[30]

* It was supposed the presence of O2, O3 and O4 in FeZnPI-56; ** It was supposed the presence of O2', O3' and O4' in FeZnPII-56.

Figure Captions

Fig. 1. Scanning electron micrographs of **2** (left) and **3** (right) crystals.

Fig. 2. The tetragonal aristotype of the DFT-zeotype structure: (a) The 3D framework of corner-sharing tetrahedra and the 8M ring channels filled with H_2en^{2+} cations when viewed approximately along [100] (+*c* direction up, +*a*₂ direction right). Hydrogen atoms were omitted because of clarity. (b) The linkage of the bhs chains built from the 4M tetrahedral rings (bold) connecting in the 3D framework viewed approximately along [100]. (c) The 4.8² 2D net perpendicular to the [001] with 4M and 8M tetrahedral rings. A trace of unit cell is drawn for reference. (d) The regular $T\text{IO}_4$ tetrahedra (PBUs) linking in 4M tetrahedral rings (SBUs) with H_2en^{2+} running along [100] and [010] in the unit cell viewed along [001]. Oxygen atoms O1 are black, O2 are dark grey and O3 are light grey. Nitrogen atoms N1 (dark grey) and the C1 atoms (light grey) of H_2en^{2+} are hatched.

Fig. 3. Two 4M tetrahedral rings (two SBUs) linked through O2 (dark grey) atoms in a double 4M ring units and two 6M rings with four common tetrahedra in the structure of (a) aristotype (*c*-axis is vertical), (b) **1**, and (c) **4**. Oxygen atoms O1 are black, O2 are dark grey and O3 are light grey. The symmetry related tetrahedra are the same color. $T'\text{O}_4$ ($T' = \text{As}$ and P in **1** and **4**, respectively) are hatched.

Fig. 4. The perspective view of the two 4M and four 8M tetrahedral rings and three mutually perpendicular channels in: (a) aristotype (lines represent the propagations of channels: channel 1 along [100] is horizontal, channel 2 along [010] is approximately normal to the plane of paper and channel 3 along [001] is vertical), (b) **1**, and (c) **4**. Oxygen atoms O1 are black, O2 are dark grey and O3 are light grey. The symmetry related tetrahedra are the same color. $T'\text{O}_4$ ($T' = \text{As}$ and P in **1** and **4**, respectively) tetrahedra are hatched.

Fig. 5. Nodal representation of the 2D 4.8² nets in the structures of (a) aristotype viewed along [001] (light grey nodes symbolize $T\text{IO}_4$ tetrahedra of aristotype), (b) **1** viewed along [001] (black and light grey nodes symbolize ZnO_4 and AsO_4 tetrahedra), (c) **4** viewed along [010] (black and light grey nodes

symbolize ZnO_4 and PO_4 tetrahedra) with selected $\text{Zn}T'\text{Zn}$ and $T'\text{Zn}T'$ angles ($T' = \text{As}$ and P in **1** and **4**, respectively).

Fig. 6. Perspective view of two possible orientations of the guest H_2en^{2+} cations: (a,b) in **1** two symmetry equivalent H_2en^{2+} ; (c,d) in **4** one ordered H_2en^{2+} in the channel 1 (vertical) and the other partly disordered in the channel 2 (horizontal). Oxygen atoms O1 are black, O2 are dark grey and O3 are light grey. The symmetry related tetrahedra are the same color. $T'\text{O}_4$ ($T' = \text{As}$ and P in **1** and **4**, respectively) as well as nitrogen atoms (black) and the C atoms (light grey) of H_2en^{2+} are hatched.

Fig. 7. Raman spectra of **1** and **4**.

Fig. 8. FTIR spectra of **2** and **3**.

Fig. 9. The Bärnighausen tree illustrating the supergroup/subgroup relationships among DFT-zeotype compounds. The left half of the three was reported earlier [2]. Space groups given in bold frames refer to the actually known crystal structures, while the others refer to the intermediate steps needed to describe the subgroup derivations. The origin shift in the group-subgroup arrow refers the coordinate system of the higher symmetry space group. All space groups are described by the subgroup relationship (*t*-subgroups from the German *translationengleiche* or *k*-subgroups from the German *klassengleiche*, which include ‘decentred’, ‘enlarged unit cell’, and ‘isomorphic’ subgroups) including the subgroup index, which represent the factor of the symmetry reduction. The Roman number I is assigned to the space group symbol of the aristotype, while the subgroups have numerals corresponding to their index of symmetry reduction relative to the aristotype. Members with the same index are drawn on the same level and are distinguished by Arabic numerals.

Fig. 10. Unit cell settings derived from aristotype in the two branches of the Bärnighausen tree shown in Fig. 6: (a) tetragonal cell in $P4_2/n$ (No. 86), (b) orthorhombic cell in $Pcca$ (No. 54). Thin lines show the 4.8^2 2D net and aristotype unit cell, while thick lines are used for unit cells of lower symmetry. The thickness of line is changed as a function of the symmetry lowering. Numbers of space groups are included.

Fig. 11. The degree of lattice distortion and the structure similarity of the DFT-zeotype structures versus average ionic radii and the ratio of ionic radii (For abbreviations and references, see Table 9).

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig 8.

Fig. 9.

a

b

Fig. 10.

Fig. 11.

Figure 1
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Figure 2
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(a)

(b)

(c)

(d)

Figure 3
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(a)

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Figure 4
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(a)

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Figure 5
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Figure 6
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(a)

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