

Quaternary Phosphide Oxides $\text{Pr}_3\text{Cu}_4\text{P}_4\text{O}_{2-x}$ and $\text{Sm}_3\text{Cu}_4\text{P}_4\text{O}_{2-x}$ with Ordered $\text{Zr}_3\text{Cu}_4\text{Si}_6$ -Type Structure

Joachim W. Kaiser and Wolfgang Jeitschko

Institut für Anorganische und Analytische Chemie, Universität Münster,
Wilhelm-Klemm-Straße 8, D-48149 Münster, Germany

Reprint requests to W. Jeitschko. E-mail: jeitsch@uni-muenster.de

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The compounds $\text{Ln}_3\text{Cu}_4\text{P}_4\text{O}_{2-x}$ ($\text{Ln} = \text{Pr}, \text{Sm}$) were prepared by annealing the elemental components in a NaCl/KCl flux. They crystallize with an ordered $\text{Zr}_3\text{Cu}_4\text{Si}_6$ -type structure (space group $I4/mmm$, $Z = 2$), which was refined from single-crystal X-ray data for both compounds; $\text{Pr}_3\text{Cu}_4\text{P}_4\text{O}_{2-x}$: $a = 397.8(1)$, $c = 2658.7(3)$ pm, $R = 0.046$ for 235 structure factors and 19 variable parameters; $\text{Sm}_3\text{Cu}_4\text{P}_4\text{O}_{2-x}$: $a = 392.8(1)$, $c = 2643.6(3)$ pm, $R = 0.057$ for 145 F values and 19 variables. The refinements showed partial occupancy for the oxygen positions resulting in approximately 1.5 oxygen atoms per formula unit. Half of the phosphorus atoms form pairs with typical two-electron bond distances of 222.8(4) and 221.7(8) pm, respectively. Using oxidation numbers chemical bonding in these phosphide oxides can be rationalized with the formula $(\text{Ln}^{+3})_3(\text{Cu}^{+1})_4(\text{P}-\text{P})^{-4}(\text{P}^{-3})_2(\text{O}^{-2})_{1.5}$. Hence, the empirical formula may also be doubled ($\text{Ln}_6\text{Cu}_8\text{P}_8\text{O}_3$), and the compounds are expected to be semiconducting.

Introduction

In recent years a new class of quaternary pnictide oxides of alkaline earth and rare earth metals with transition metals has emerged. They have relatively simple tetragonal or hexagonal structures with a more or less layered character and relatively long c axes. The tetragonal manganese compounds $\text{A}_2\text{Mn}_3\text{Pn}_2\text{O}_2$ ($\text{A} = \text{Sr}, \text{Ba}$; $\text{Pn} = \text{P}, \text{As}, \text{Sb}, \text{Bi}$) [1–4], the isotypic zinc compounds $\text{A}_2\text{Zn}_3\text{As}_2\text{O}_2$ ($\text{A} = \text{Sr}, \text{Ba}$) [5], and the hexagonal compounds $\text{Ba}_2\text{Mn}_2\text{Pn}_2\text{O}$ ($\text{Pn} = \text{Sb}, \text{Bi}$) [6] were the first ones to be prepared [7]. The arsenide oxide $\text{Ba}_2\text{Mn}_2\text{As}_2\text{O}$ has a monoclinic structure [8]. Three different, closely related tetragonal structures have been reported for the uranium and thorium compounds $\text{U}_2\text{Cu}_2\text{P}_3\text{O}$ [9, 10], $\text{U}_2\text{Cu}_2\text{As}_3\text{O}$ [10], and $\text{Th}_2\text{Ni}_{3-x}\text{P}_3\text{O}$ [11].

The quaternary pnictide oxides with the most simple structures are the equiatomic compounds UCuPO [12], ThCuPO and ThCuAsO [11], and the lanthanoid transition metal phosphide oxides LnTPO ($T = \text{Fe}, \text{Ru}, \text{Co}$) [13], AMnPnO ($\text{A} = \text{rare earth elements and uranium}, \text{Pn} = \text{P}, \text{As}, \text{Sb}$) [14], LnZnPnO ($\text{Pn} = \text{P}, \text{As}, \text{Sb}$) [15, 16], and LnTAsO ($T = \text{Fe}, \text{Ru}, \text{Os}$) [17]. They crystallize with the tetragonal ZrCuSiAs (filled PbFCl)

type structure [18]. This structure has also been found for equiatomic sulfide oxides and selenide oxides, e.g., LaTSO ($T = \text{Cu}, \text{Ag}$) [19–21] and ACuSeO ($\text{A} = \text{Bi}, \text{Ln}$) [22], of which the silver containing compound LaAgSO is a solid electrolyte [19, 20], while the equiatomic phosphide oxides with small rare earth atoms AZnPO ($\text{A} = \text{Y}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd-Tm}$) crystallize with a very simple hexagonal structure [16]. In contrast, the compounds $\text{Na}_3\text{Sr}_7\text{P}_9\text{O}$ and $\text{Na}_3\text{Eu}_7\text{P}_9\text{O}$ are polyphosphide oxides [23], while $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}$ is better designated as a phosphide suboxide [24].

The compounds $\text{Pr}_3\text{Cu}_4\text{P}_4\text{O}_{2-x}$ and $\text{Sm}_3\text{Cu}_4\text{P}_4\text{O}_{2-x}$ characterized here have the same crystal structure as reported for the phosphide oxides $\text{Ln}_3\text{Cu}_4\text{P}_4\text{O}_2$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Nd}$). The structure of these compounds was determined from single-crystal X-ray data of the lanthanum compound, where a relatively large displacement parameter was observed for the oxygen position [25]. This crystal structure has the same space group symmetry and occupied atomic positions as that of $\text{Zr}_3\text{Cu}_4\text{Si}_6$ [26]. It may therefore be considered as isotypic, however, since chemical bonding in the ternary silicide is different, the expression “isopointal” may be more appropriate [27].

Compound	<i>a</i> [pm]	<i>c</i> [pm]	<i>V</i> [nm ³]	Ref.
La ₃ Cu ₄ P ₄ O ₂	403.3(1)	2676.5(8)	0.4353	[25]
Ce ₃ Cu ₄ P ₄ O ₂	398.5(1)	2657.3(9)	0.4220	[25]
Pr ₃ Cu ₄ P ₄ O _{2-x}	397.8(1)	2658.7(3)	0.4207	this work
Nd ₃ Cu ₄ P ₄ O ₂	396.4(1)	2655.1(5)	0.4172	[25]
Sm ₃ Cu ₄ P ₄ O _{2-x}	392.8(1)	2643.6(3)	0.4079	this work

Table 1. Lattice constants of the compounds Ln₃Cu₄P₄O_{2-x} (Ln = La-Nd, Sm) with ordered Zr₃Cu₄Si₆-type structure. Standard deviations are listed in parentheses throughout the paper; they correspond to the last printed digits.

Composition	Pr ₃ Cu ₄ P ₄ O _{1.50(4)}	Sm ₃ Cu ₄ P ₄ O _{1.63(6)}
Molar mass	824.8	855.5
Lattice constants: <i>a</i> [pm]	397.5(1)	392.4(1)
<i>c</i> [pm]	2658.3(4)	2643.2(9)
<i>V</i> [nm ³]	0.4200	0.4070
Calculated density [g/cm ³]	6.52	6.98
Crystal size [μm]	10 × 30 × 40	40 × 50 × 50
Transmission ratio (max/min)	1.13	1.11
Scans up to 2θ [°]	70	60
Range in <i>h, k, l</i>	±6, ±6, 0-42	±5, ±5, 0-37
Total number of reflections	3419	1101
Independent reflections	325	214
Internal residual, <i>R</i> _{int} (all <i>F</i>)	0.052	0.071
Reflections with <i>I</i> ₀ > 2σ(<i>I</i> ₀)	235	145
Number of variables	19	19
Conventional residual, <i>R</i> (<i>F</i> > 2σ)	0.046	0.057
Weighted residual, <i>R</i> _w (all <i>F</i> ² > 2σ)	0.128	0.160
Largest difference peak/hole [e/Å ³]	6.4/-4.8	7.4/-3.3

Table 2. Crystallographic data for Pr₃Cu₄P₄O_{2-x} and Sm₃Cu₄P₄O_{2-x} with ordered Zr₃Cu₄Si₆-type structure (space group *I4/mmm*, No. 139, *Z* = 2, Pearson code [28] *t*/26).

Experimental Section

Sample preparation, properties, and lattice constants

The rare earth elements praseodymium and samarium were purchased in the form of ingots (Kelpin, 99.9%). Filings were prepared under dry (Na) paraffin oil, washed with dry hexane, stored in vacuum, and not exposed to air prior to the reactions. Powders of copper (Merck, > 99.7%), copper(II) oxide (Merck, > 99%) and phosphorus (Hoechst, ultrarein) were used as purchased. The compounds were prepared in a salt flux (NaCl / KCl = 1 : 1). The components were mixed in the atomic ratio Ln : Cu : CuO : P = 3 : 2 : 2 : 4 and sealed under vacuum into silica tubes together with approximately the fivefold amount (in weight) of the flux. The samples were annealed for 1 d at 500 °C, followed by 10 d at 800 °C. The salt flux probably only partially dissolves the metallic components. Thus, it essentially serves as a reaction medium. The tubes were then quenched in air, and the salt matrix was dissolved in water.

The compounds are stable in air for long periods of time. The crystals have metallic luster; the powders are dark gray. Energy-dispersive X-ray fluorescence analyses (EDX) in a scanning electron microscope did not show any impurity elements heavier than sodium.

The lattice constants were obtained by least-squares fits of Guinier powder data using Cu-*K*_{α1} radiation and

α-quartz (*a* = 491.30 pm, *c* = 540.46 pm) as an internal standard. The lattice constants are listed in Table 1 together with those of the three isotopic compounds prepared by Cava *et al.* [25].

Structure refinements

Single crystals of Pr₃Cu₄P₄O_{2-x} and Sm₃Cu₄P₄O_{2-x} were examined with a Buerger precession camera to establish their suitability for the intensity data collection. These data were recorded on an automated four-circle diffractometer with graphite-monochromated Mo-*K*_α radiation and a scintillation counter with pulse-height discrimination. The background was determined at both ends of each θ/2θ scan. Empirical absorption corrections were applied from psi scan data. Further details are summarized in Table 2.

The structure of the two new compounds was assumed to be isotopic with La₃Cu₄P₄O₂ [25] and this was confirmed by the structure refinement with a full-matrix least-squares program using atomic scattering factors, corrected for anomalous dispersion as provided by the program [29]. The weighting scheme accounted for the counting statistics, and a parameter correcting for isotropic secondary extinction was optimized as a least-squares variable. As a check for the composition we refined occupancy parameters together with the displace-

Atom	<i>I4/mmm</i>	Occup.	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}/B</i>
Pr₃Cu₄P₄O_{1.50(4)}						
Pr1	4 <i>e</i>	1.00(1)	0	0	0.29697(2)	0.54(1)
Pr2	2 <i>a</i>	0.99(1)	0	0	0	0.29(1)
Cu	8 <i>g</i>	1.00(1)	0	1/2	0.09474(3)	0.73(1)
P1	4 <i>e</i>	0.99(1)	0	0	0.14172(8)	0.46(4)
P2	4 <i>e</i>	0.99(1)	0	0	0.45811(8)	0.29(3)
O	4 <i>d</i>	0.75(2)	0	1/2	1/4	0.3(1)
Sm₃Cu₄P₄O_{1.63(6)}						
Sm1	4 <i>e</i>	0.99(1)	0	0	0.29570(3)	0.57(1)
Sm2	2 <i>a</i>	0.99(1)	0	0	0	0.43(2)
Cu	8 <i>g</i>	1.00(1)	0	1/2	0.09557(5)	0.75(3)
P1	4 <i>e</i>	0.98(1)	0	0	0.1435(2)	0.52(7)
P2	4 <i>e</i>	1.01(1)	0	0	0.4581(2)	0.27(7)
O	4 <i>d</i>	0.82(3)	0	1/2	1/4	0.7(2)

<i>Ln</i> 1:	4O	234.9/230.6	Cu:	2P1	234.9/233.8
	4P1	325.1/320.9		2P2	243.5/242.2
	4Cu	350.0/348.1		4Cu	281.3/277.8
	(4 <i>Ln</i> 1	376.2/368.1)		2 <i>Ln</i> 2	321.0/320.0
	(4 <i>Ln</i> 1	397.8/392.8)		2 <i>Ln</i> 1	350.0/348.1
<i>Ln</i> 2:	8P2	302.5/299.1	P1:	4Cu	234.9/233.8
	8Cu	320.9/320.0		4 <i>Ln</i> 1	325.1/320.9
	(2P1	376.8/379.5)		(1 <i>Ln</i> 1	376.8/379.5)
	(4 <i>Ln</i> 2	397.8/392.8)	P2:	1P2	222.8(4)/221.7(8)
O:	4 <i>Ln</i> 1	234.9/230.6		4Cu	243.5/242.2
				4 <i>Ln</i> 2	302.5/299.1

ment parameters, while the scale factor was held constant. For both compounds significant deviations from the ideal occupancy values were found only for the oxygen position (Table 3). Thus, in the final refinement cycles we resumed to the ideal occupancies for the other positions, while the oxygen occupancy was variable. The final difference Fourier analyses showed as highest residual peaks electron densities of 6.4 and 7.4 e/Å³ for the praseodymium and samarium compounds, respectively. These were in the vicinity of fully occupied atomic sites and therefore they are not suited for additional atomic positions. The final atomic parameters and the interatomic distances are listed in the Tables 3 and 4. The crystallographic data have been deposited. They may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) by quoting the registry numbers CSD-412191 (Pr₃Cu₄P₄O_{2-x}) and CSD-412192 (Sm₃Cu₄P₄O_{2-x}).

Discussion

The five phosphide oxides *Ln*₃Cu₄P₄O_{2-x} with La₃Cu₄P₄O₂ type structure are represented by their

Table 3. Atomic parameters for the compounds Pr₃Cu₄P₄O_{1.50(4)} and Sm₃Cu₄P₄O_{1.63(6)}. The positional parameters were standardized using the program STRUCTURE TIDY [27]. The occupancy parameters were refined in separate series of least-squares cycles. In the final cycles the ideal occupancies were assumed with the exception of those for the oxygen positions, where the presently listed values were obtained. All atoms were refined with anisotropic displacement parameters with the exception of those for the oxygen atoms. The equivalent isotropic displacement parameters *B_{eq}* and the isotropic displacement parameters *B* of the oxygen atoms are given in units of Å².

Table 4. Interatomic distances in the structures of *Ln*₃Cu₄P₄O_{2-x} with *Ln* = Pr/Sm. The distances were calculated using the lattice constants as obtained from the Guinier powder data. All distances shorter than 400 pm (*Ln* atoms), 390 pm (Cu atoms), 340 pm (P-P and P-O distances), 270 pm (O-O), respectively, are listed. The standard deviations are all 0.2 pm or less, with the exception of the P2-P2 distances where they are listed. Atoms with distances listed in parentheses are not shown as neighbors in Fig. 2.

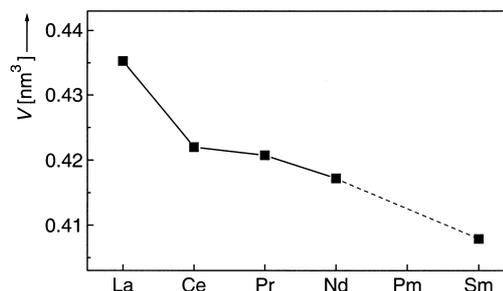


Fig. 1. Cell volumes of the compounds of *Ln*₃Cu₄P₄O_{2-x}.

cell volumes in Fig. 1. The cell volume of the cerium compound slightly deviates from the smooth function found for the volumes of the typically trivalent rare earth elements, thus indicating that cerium in this compound is partially tetravalent. A much smaller cell volume would be expected if cerium were fully tetravalent.

Our structure refinements for the new compounds Pr₃Cu₄P₄O_{2-x} and Sm₃Cu₄P₄O_{2-x} resulted in considerable deviations from the full occupancy values for the oxygen positions. As is discussed further below, the ideal occupancy value for the oxygen

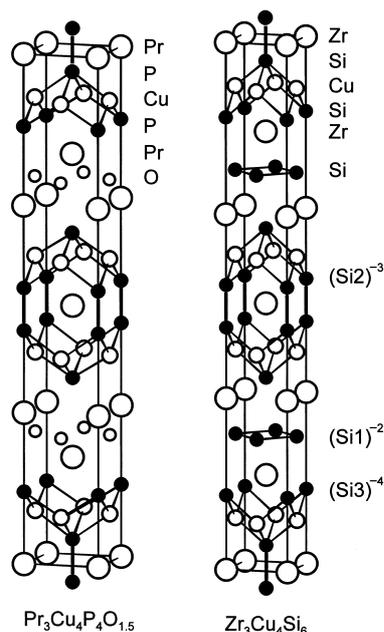


Fig. 2. The structure of $\text{Pr}_3\text{Cu}_4\text{P}_4\text{O}_{1.5}$ as compared to the structure of $\text{Zr}_3\text{Cu}_4\text{Si}_6$. For the latter structure the silicon atoms are indicated with their formal charges.

position of the compounds with trivalent rare earth elements may well be 75%, corresponding to the formula $\text{Ln}_6\text{Cu}_8\text{P}_8\text{O}_3$. The structure refinement of $\text{La}_3\text{Cu}_4\text{P}_4\text{O}_2$ by Cava *et al.* [25] resulted in a rather large displacement parameter, $B = 3.3(9) \text{ \AA}^2$, for the oxygen position, as compared to the other parameters B which varied between $0.3(2) \text{ \AA}^2$ for one of the phosphorus positions and $0.90(7) \text{ \AA}^2$ for one of the lanthanum sites. This suggests that the oxygen position in this compound may as well not be fully occupied.

We have searched the TYPIX compilation by Parthé *et al.* [28] in looking for isotopic compounds, where we found the ternary zirconium copper silicide with the total cell content of $\text{Zr}_6\text{Cu}_8\text{Si}_{12}$ [26]. The two isotopic tetragonal structures are compared to each other in Fig. 2. The correspondence of the atomic sites of the two structures becomes apparent by the crystal chemical formulas $(\text{Pr}1)_4(\text{Pr}2)_2\text{Cu}_8(\text{P}1)_4(\text{P}2)_4\text{O}_{4-x}$ and $(\text{Zr}2)_4(\text{Zr}1)_2\text{Cu}_8(\text{Si}3)_4(\text{Si}2)_4(\text{Si}1)_4$. The structure of these compounds belongs to a large family of tetragonal structures. Several of these have been enumerated above [1 - 5, 9 - 22]. Some others, which do not contain oxygen, have been cited in publications on $\text{U}_3\text{Ni}_{3.34}\text{P}_6$ [30] and $\text{PrCr}_2\text{Si}_2\text{C}$ [31].

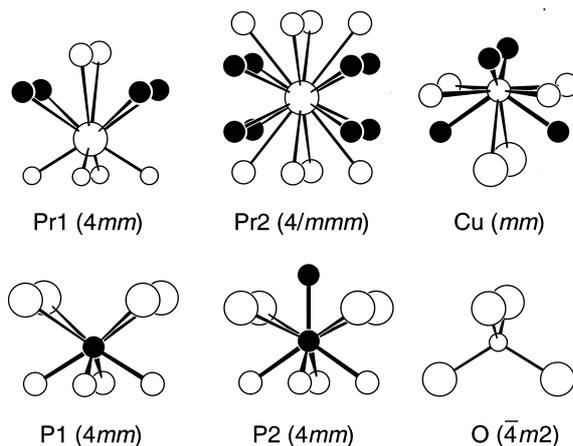


Fig. 3. Near-neighbor coordinations in the structure of $\text{Pr}_3\text{Cu}_4\text{P}_4\text{O}_{2-x}$. The site symmetries of the central atoms are given in parentheses.

We will briefly discuss chemical bonding in the rare earth copper phosphide oxides with $\text{Pr}_3\text{Cu}_4\text{P}_4\text{O}_{2-x}$ as an example, using oxidation numbers (formal charges), where the more or less covalently bonding electrons are counted at the atoms with the higher electronegativity. The near-neighbor environments in the structure of $\text{Pr}_3\text{Cu}_4\text{P}_4\text{O}_{1.5}$ are shown in Fig. 3. For the praseodymium atoms we can assume the oxidation number +3 as is indicated by the volume plot (Fig. 1). The oxygen atoms have only four praseodymium neighbors in tetrahedral coordination, they thus obtain the oxidation number -2 . Of the two different phosphorus atoms, the P1 atoms have no phosphorus neighbors, and we may safely assume that they use only their $3s$ and $3p$ orbitals for bonding (octet rule). Since there are no phosphorus-oxygen bonds, they obtain the oxidation number -3 . In contrast, the P2 atoms form pairs with the P-P distance of $222.8(4) \text{ pm}$. This is a typical two-electron bond distance, found also in the various modifications of elemental phosphorus [32]. Therefore, the P2 atoms must be assigned the oxidation number -2 . The oxidation number of the copper atoms is then obtained by balancing the formal charges, and accounting for the partial occupancy of the oxygen position, we obtain for the total content of the unit cell the formula $(\text{Pr}^{+3})_6(\text{Cu}^{+1})_8(\text{P}1^{-3})_4(\text{P}2^{-2})_4(\text{O}^{-2})_3$. Thus, we observe reasonable oxidation numbers for all atoms and we expect semiconductivity for this compound as is observed for many polyphosphides, *e. g.* for Cu_2P_7 [33].

As already mentioned above, the cell volumes (Fig. 1) indicated the cerium atoms in $\text{Ce}_3\text{Cu}_4\text{P}_4\text{O}_{2-x}$ to have mixed or intermediate $\text{Ce}^{+3/+4}$ valence. There are two possibilities to balance the charges. One would be to elongate the P-P bond of the P2 atoms. (They have a charge of -2 if they form pairs, and a charge of -3 if they are isolated from each other. With an elongated P2-P2 bond their oxidation number would be between -2 and -3 .) Another possibility would be to increase the occupancy of the oxygen position. This second possibility seems to us to be more plausible, since i) the oxygen positions are in the immediate neighborhood of the rare earth positions and since ii) fractional P-P bonds are rare, in contrast to fractional Sb-Sb bonds [34].

In conclusion, we will briefly consider chemical bonding in the isopointal compound $\text{Zr}_3\text{Cu}_4\text{Si}_6$ [26]. The zirconium atoms are the most electropositive components in this compound, and they do not form any Zr-Zr bonds. They are coordinated only by silicon and copper atoms, and we have to count their valence electrons at these neighbors. The Si1 atoms form weak Si1-Si1 bonds of 264.3 pm. In aiming for simplicity, we can count these as one-electron bonds. The Si1 atoms then obtain a formal charge of -2 , being in between elemental silicon (with the diamond structure) with four near silicon neighbors at 235.2 pm and isolated silicon atoms, which by definition (as the most electronegative atoms of the compound) obtain a formal charge of -4 . The Si2 atoms of $\text{Zr}_3\text{Cu}_4\text{Si}_6$ are forming pairs with a Si2-Si2 distance of 229(1) pm, close to the two-electron bond distance of 235.2 pm. We therefore assign an oxidation number of -3 to these atoms. Finally, the Si3 atoms of $\text{Zr}_3\text{Cu}_4\text{Si}_6$ are isolated from each other, thus resulting in the oxidation number -4 .

The oxidation number for the copper atoms, which occupy only one site, is obtained by balancing the formal charges. For the total cell content we then arrive at the formula $(\text{Zr}^{+4})_6(\text{Cu}^{+1.5})_8(\text{Si1}^{-2})_4(\text{Si2}^{-3})_4(\text{Si3}^{-4})_4$. Hence, we obtain an oxidation number of $+1.5$ for the copper atoms, in contrast to the oxidation number of $+1$ obtained for the copper atoms in the quaternary phosphide oxides $\text{Ln}_3\text{Cu}_4\text{P}_4\text{O}_{2-x}$ of the present paper. The difference in the oxidation numbers of the copper atoms is evidenced in the shortest Cu-Cu distances. In the compounds $\text{Pr}_3\text{Cu}_4\text{P}_4\text{O}_{2-x}$ and $\text{Sm}_3\text{Cu}_4\text{P}_4\text{O}_{2-x}$ these distances are relatively long with 281.3(1) and 277.8(1) pm. They may be considered as marginally bonding. On the contrary, in $\text{Zr}_3\text{Cu}_4\text{Si}_6$ each copper atom has four copper neighbors with a (weakly) bonding Cu-Cu distance of 264.3(1) pm, as compared to the bonding Cu-Cu distance of 255.5 pm in elemental copper [32].

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Note added in proof. With respect to the pnictide oxides mentioned in the introduction we wish to draw the attention of the reader also to recent publications on the ZrCuSiAs -type compounds LaCdPO and LnCdAsO ($\text{Ln} = \text{La} - \text{Nd}$) [35], $\text{Ba}_2\text{MnZn}_2\text{As}_2\text{O}_2$ [36] with ordered $\text{Sr}_2\text{Mn}_3\text{As}_2\text{O}_2$ -type structure [1], and on the compounds $\text{Na}_2\text{Ti}_2\text{Pn}_2\text{O}$ ($\text{Pn} = \text{As}, \text{Sb}$) with trivalent titanium [37 - 39].

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