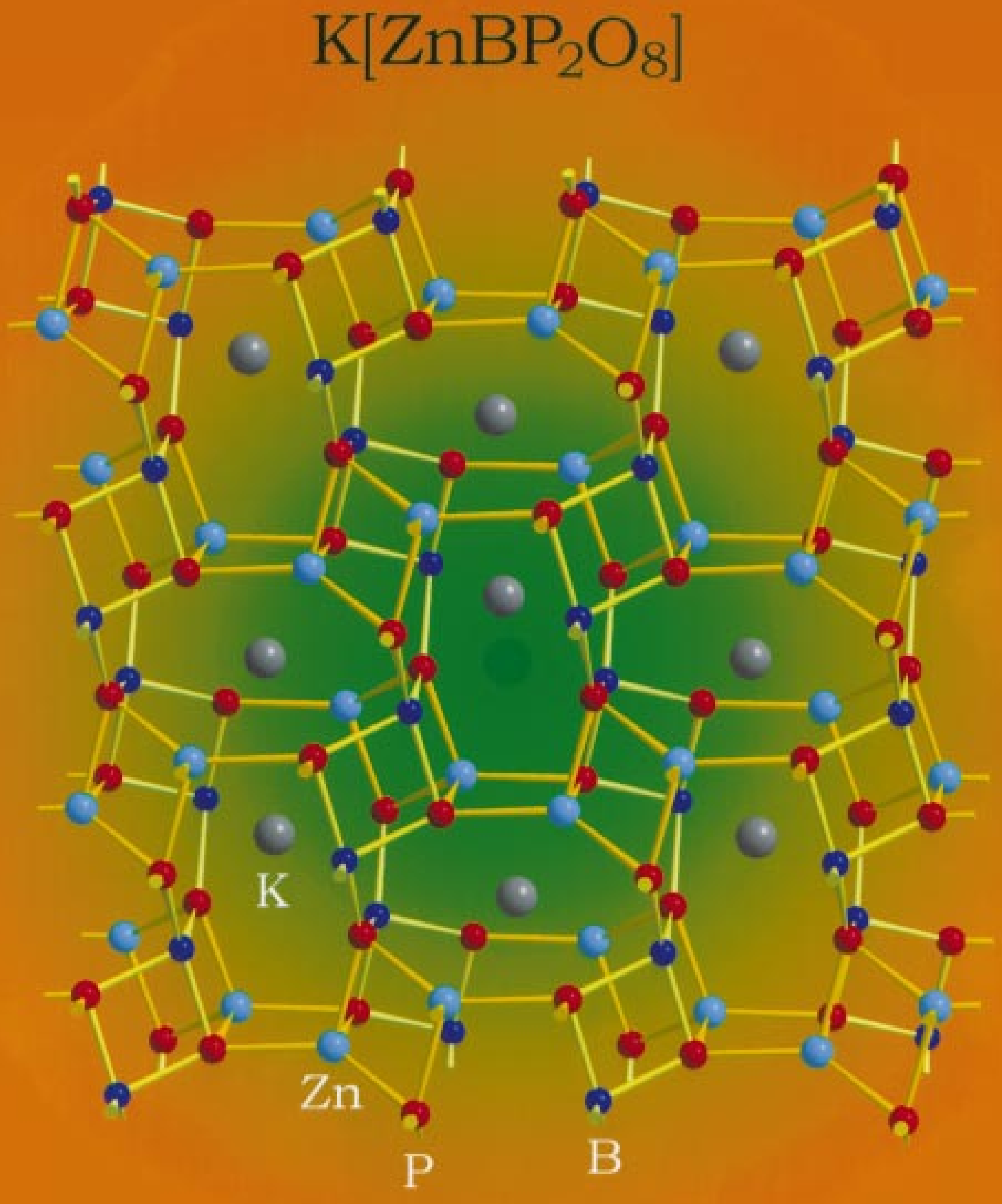

Metalloborophosphates provide access to new systems with microporous structures. The tetrahedral framework structures of zincoborophosphates display a close relationship to topolgies of the anionic partial structures in feldspars and gismondine. Find out more on the following pages.

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$K[ZnBP_2O_8]$ and $A[ZnBP_2O_8]$ ($A = NH_4^+$, Rb^+, Cs^+): Zincoborophosphates as a New Class of Compounds with Tetrahedral Framework Structures**

Rüdiger Kniep,* Gerd Schäfer, Holger Engelhardt, and Insan Boy

Materials based on aluminosilicate cage structures (e.g. the zeolite family) have been studied for some time from various standpoints in view of their potential applications as catalysts, molecular sieves, and ion exchangers.[1] In the last few years the interest in microporous and zeolite-analogous systems has focused primarily on aluminum phosphates[2] and substituted variants[3] as well as on zinco-,[4] beryllo-,[5] gallium/gallo-,[6] and zincogallophosphates.[7] A microporous zincoborate[8] is also known. In contrast, borophosphates have only recently been studied systematically.[9] This is remarkable, since the effect of the substitution of aluminum and/or silicon by boron in zeolitic molecular sieves, such as in the boron/MFI-zeolite, has long been known in technical processes.[10]

Our studies aimed at the systematic development of the structural chemistry of the borophosphates[11] have led to a broad spectrum of new compounds with quite different anionic partial structures, such as oligomeric units,[12] chains,[9, 13] ribbons,[14] layers,[15] and three-dimensional frameworks.[16] In water-containing borophosphates with chain structures and molar B:P ratios of >1, boron is both tetrahedrally and trigonal-planar coordinated by oxygen.[11, 13] With the synthesis of $K[ZnBP_2O_8]$ and $A[ZnBP_2O_8]$ ($A = NH_4^+$, Rb^+, Cs^+)[17] we have now succeeded in extending the chemical diversity of compounds with tetrahedral framework structures. The zincoborophosphates presented here contain tetrahedral nets, whose topologies display a close relationship to tecto-aluminosilicates (feldspar family and gismondine).

The characteristic basic units in the crystal structures of $K[ZnBP_2O_8]$ and $A[ZnBP_2O_8]$ ($A = NH_4^+$, Rb^+, Cs^+)[18] are based on four-rings, which contain corner-sharing borate, phosphate, and zincate tetrahedra. These occur in three ordered variants (Figure 1, right): four-rings from two borate and two phosphate tetrahedra, from two phosphate and two zincate tetrahedra, or from one borate, one zincate, and two phosphate tetrahedra; a linkage of borate and zincate tetrahedra is avoided. All four-ring systems display, with respect to the alignment of the vertices, the conformation UUDD (up-up-down-down). Four-ring building blocks of this general type are denoted as secondary building units (SBU) and form the basis of the structural chemistry of a large group of tecto-aluminosilicates, among which are the feldspars.[19] Bond lengths and angles of the BO_4, PO_4, and ZnO_4 groups in the title compounds are similar to known values in zincophosphates[4] and borophosphates.[20]

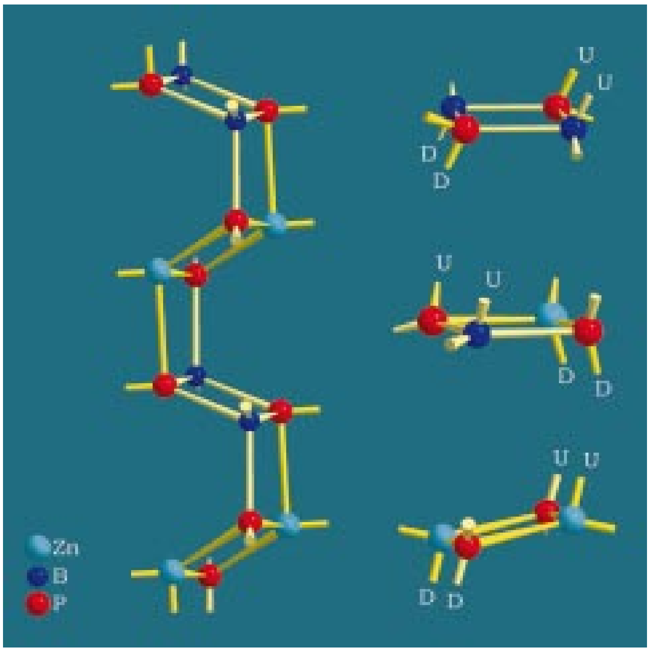

Figure 1. Topology, conformation, and linkage of tetrahderal four-ring centers in zincoborophosphates. Right: Four-rings in the crystal structures of $K[ZnBP_2O_8]$ and $A[ZnBP_2O_8]$ ($A = NH_4^+$, Rb^+, Cs^+). Left: Crankshaft-like four-ring ribbons that occur in both crystal structures. See text for further details.

The linkage of the four-ring systems with each other leads in an initial formal step to 4.8^2 nets,[21] from which the topology of the networks can be derived. The complex framework in the crystal structures of the isotypic compounds $A[ZnBP_2O_8]$ ($A = NH_4^+$, Rb^+, Cs^+) contains a conformation pattern of the 4.8^2 nets, which is also present in gismondine ($Ca[Al_2Si_2O_8] \cdot 4H_2O$).[22] Here, only the four-rings $\overline{\text{Zn-P-Zn-P}}$ and $\overline{\text{P-B-P-B}}$ participate in the formation of the nets, which are then linked through zincate with phosphate and through borate with phosphate tetrahedra, respectively. Four-rings with three different tetrahedral centers $\overline{\text{Zn-P-B-P}}$ result from the linkage of the nets with each other. Additional building units resulting from this mode of linkage are crankshaft-like four-ring ribbons, which run along [101] (Figure 1, left). Figure 2 shows the three-dimensional structural framework as exemplified by $NH_4[ZnBP_2O_8]$ as well as the characteristic 4.8^2 nets with gismondine topology (IZA structure designation GIS).[23] Along [101] the nets are linked with each other in an ABAB sequence. The resulting network is evidently very flexible and is realized in a large number of different compounds, such as SAPO-43,[24] NaP-[25] and CaP-zeolites,[26] and zincogallophosphates (T)$[ZnGaP_2O_8]$ ($T = CN_3H_5$ and C_4NH_9).[27] The minimum/maximum opening areas of the eight-rings (distances O⋯O) are 351/896 (NH_4 phase), 308/885 (Rb phase), and

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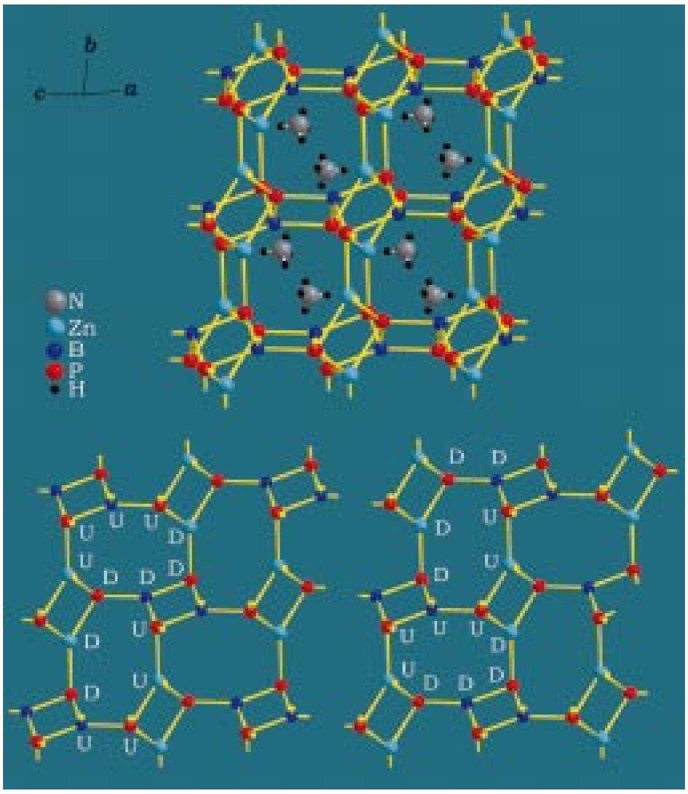

Figure 2. Gismondine-analogous linkage of tetrahdral centers in the crystal structure of $NH_4[ZnBP_2O_8]$. Top: Topology of the framework structure (view approximately along [101]). Bottom: 4.8^2 nets. See text for further details.

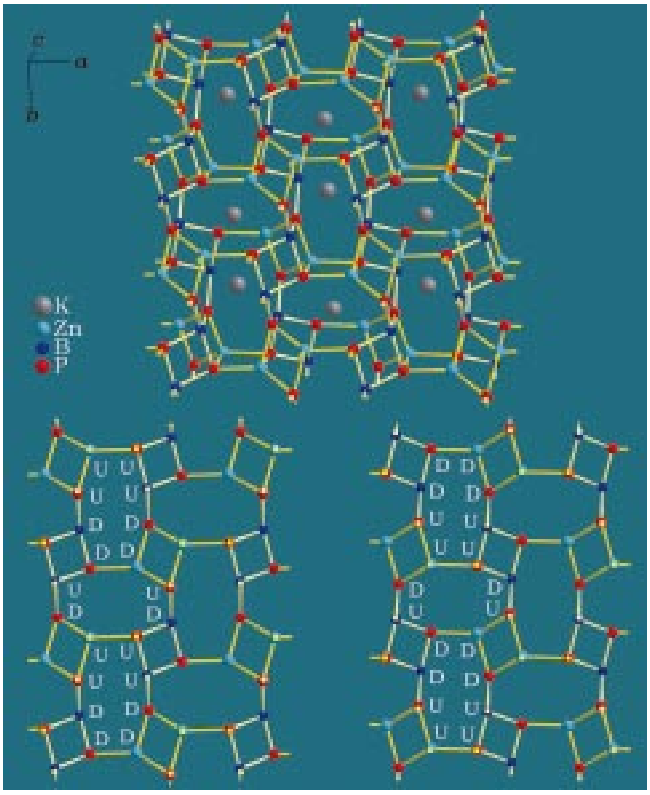

Figure 3. The crystal structure of $K[ZnBP_2O_8]$. Top: Topology of the framework structure (linkage of the tetrahedral centers). Bottom: feldspar-analogous 4.8^2 nets. See text for further details.

313/891 pm (Cs phase). Rb^+ and Cs^+ ions in the cavities are surrounded by seven oxygen atoms, giving rise to irregular polyhedra. In the crystal structure of the ammonium compound hydrogen bonds N–H···O (N···O 288–307 pm) fix the complex cation to the oxygen sites of adjacent tetrahedra. The tetrahedral network density (framework density (FD): number of tetrahedrally coordinated atoms in a volume of 1000 Å³)[28] of the isotypic compounds lies in the range between 21.4 and 22.8, and thus resembles the framework density of cristobalite (23.0).[29] Difference thermoanalytical/thermogravimetric studies (Netzsch STA 409EP, heating rate 5 $K\,min^{-1}$, open system in air) indicate a remarkable thermal stability of the compounds: 480 °C ($NH_4[ZnBP_2O_8]$), 850 °C ($Rb[ZnBP_2O_8]$), and 940 °C ($Cs[ZnBP_2O_8]$).

The crystal structure of $K[ZnBP_2O_8]$ can be described starting from 4.8^2 nets with feldspar topology. As in the previously discussed compounds these nets from four-rings $\overline{\text{Zn-P-Zn-P}}$ and $\overline{\text{P-B-P-B}}$ are formally used for the framework construction. Figure 3 shows the three-dimensional framework of $K[ZnBP_2O_8]$ as well as the characteristic 4.8^2 nets with feldspar topology, whose elliptical eight-ring systems are built from four phosphate, two borate, and two zincate tetrahedra. The linkage of the nets along [001] corresponds to the sequence $A\bar{A}A\bar{A}$, where $\bar{A}$ is the symbol for an inverted net. The special nature of the linkage leads to eight-ring channels, in which the potassium ions are irregularly surrounded by eight or ten oxygen neighbors. Also in this case crankshaft-like four-ring ribbons result, which run along [001] (Figure 1, left). The network linkage $A\bar{A}A\bar{A}$ is new. In the feldspar family (e.g. anorthite ($Ca[Al_2Si_2O_8]$))[30] the 4.8^2 nets are linked according to an ABAB pattern. The minimum/maximum opening area of the elliptical eight-rings of $K[ZnBP_2O_8]$ (distances O···O) is 296/930 pm. The tetrahedral network density (see above) of $K[ZnBP_2O_8]$ is 23.6. The compound is thermally stable up to 822 °C.

Based on the compounds presented it becomes clear that with metalloborophosphates anionic partial structures can be realized, which open the door to real microporous systems. Also of significance is that the elements participating in the anionic structures are distributed in an ordered fashion. The next generations of this class of compounds will probably contain redox-active transition metals. In addition the possibility of integrating three-coordinate boron in the anionic partial structures should be kept in mind.

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[17] The title compounds $K[ZnBP_2O_8]$ and $A[ZnBP_2O_8]$ ($A = NH_4^+$, Rb^+, Cs^+) were prepared under mild hydrothermal conditions in teflon autoclaves (internal volume 20 mL). For this the starting materials (see below) were heated to about 80°C in demineralized water (10 mL) and treated under stirring with 85% H_3PO_4, until the components had dissolved completely. The clear solutions were concentrated to about 15–20 mL to give a highly viscous gel. The pH values were between 1 and 1.5. The highly viscous gels were transferred to the teflon autoclaves (degree of filling about 60–80%) and stored for three to four days at about 170°C. The crystalline reaction products were filtered off in vacuo, washed with demineralized water, and dried at 60°C. Single crystals with an approximate monoclinic habit grow to a length of about 0.8 mm under these conditions. Starting materials used for the syntheses: a) $K[ZnBP_2O_8]$: 0.65 g ZnO, 2.44 g $K_2B_4O_7 \cdot 4H_2O$, 2.2 g K_2HPO_4 (molar ratio 1:1:2), 5.5 mL 85% H_3PO_4, degree of filling 60%; b) $NH_4[ZnBP_2O_8]$: 2.33 g ZnO, 0.99 g B_2O_3, 7.55 g $(NH_4)_2HPO_4$ (molar ratio 2:1:4), 6 mL 85% H_3PO_4, degree of filling 70%; c) $Rb[ZnBP_2O_8]$: 7.62 g RbOH, 3.02 g ZnO, 1.29 g B_2O_3 (molar ratio 2:2:1), 9 mL 85% H_3PO_4, degree of filling 65%; d) $Cs[ZnBP_2O_8]$: 8.6 g CsOH, 2.33 g ZnO, 0.99 g B_2O_3, (molar ratio 2:2:1), 7.1 mL 85% H_3PO_4, degree of filling 90%.

[18] a) Crystal structure determinations: Diffractometer: Philips PW 1100 (modernized by Stoe) for $K[ZnBP_2O_8]$, Siemens P4 for $A[ZnBP_2O_8]$ ($A = NH_4^+$, Rb^+, Cs^+); $Mo_{K\alpha}$ radiation; graphite monochromator; measurement range $5 \leqslant 2\theta \leqslant 60$; Lorentzian, polarization, and absorption (Ψ scan) corrections; structures solved by direct methods and refined by full-matrix least-squares methods by using the SHELX-97 program (G. M. Sheldrick, SHELX-97, Universität Göttingen, **1997**); anisotropic displacement parameters (except for N and H). The positions of the H atoms in $NH_4[ZnBP_2O_8]$ were obtained from difference-Fourier syntheses, refinement with restraints (N–H distances to 0.86 Å, H-N-H angle approximately the tetrahedral angle and $U_{iso}(H) = 1.2\ U_{iso}(N)$). b) Crystal structure data: 1) $K[ZnBP_2O_8]$: monoclinic, space group $C2/c$ (no. 15), $a = 1261.7(5)$, $b = 1277.3(6)$, $c = 841.5(3)$ pm, $\beta = 91.25(3)°$, $V = 1355.8(1)$ Å^3, $Z = 8$, $\rho_{calcd} = 2.991\ g\,cm^{-3}$; $\mu(Mo_{K\alpha}) = 4.72\ mm^{-1}$; 4110 measured reflections, 1978 independent reflections, 1586 with $F_o > 4\sigma(F_o)$; 119 free parameters; GOF = 0.954; R values for $F_o > 4\sigma(F_o)$: $R1 = 0.0273$, $wR2 = 0.0630$; max./min. residual electron density: $0.519/-0.554 \times 10^{-6}\ e\,pm^{-3}$. 2) $A[ZnBP_2O_8]$ ($A = NH_4^+$, Rb^+, Cs^+): triclinic, space group $P\bar{1}$ (no. 2); $NH_4[ZnBP_2O_8]$: $a = 743.7(1)$, $b = 761.2(1)$, $c = 785.0(1)$ pm, $\alpha = 119.05(2)$, $\beta = 101.59(1)$, $\gamma = 103.43(1)°$, $V = 351.18(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.687\ g\,cm^{-3}$; $\mu(Mo_{K\alpha}) = 3.969\ mm^{-1}$; 4758 measured reflections, 1968 independent reflections, 1892 with $F_o > 4\sigma(F_o)$; 121 free parameters; GOF = 1.162; R values for $F_o > 4\sigma(F_o)$: $R1 = 0.0224$, $wR2 = 0.0628$; max./min. residual electron density: $0.801/-0.720 \times 10^{-6}\ e\,pm^{-3}$. $Rb[ZnBP_2O_8]$: $a = 743.9(2)$, $b = 763.9(2)$, $c = 786.1(2)$ pm, $\alpha = 118.82(2)$, $\beta = 101.73(2)$, $\gamma = 103.51(2)°$, $V = 353.4(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 3.304\ g\,cm^{-3}$; $\mu(Mo_{K\alpha}) = 10.779\ mm^{-1}$; 3752 measured reflections, 1878 independent reflections, 1616 with $F_o > 4\sigma(F_o)$; 118 free parameters; GOF = 1.073; R values for $F_o > 4\sigma(F_o)$: $R1 = 0.0283$, $wR2 = 0.0674$; max./min. residual electron density: $1.63/-1.04 \times 10^{-6}\ e\,pm^{-3}$. $Cs[ZnBP_2O_8]$: $a = 750.6(2)$, $b = 791.4(2)$, $c = 803.8(2)$ pm, $\alpha = 118.05(2)$, $\beta = 102.96(2)$, $\gamma = 104.50(2)°$, $V = 373.9(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 3.545\ g\,cm^{-3}$; $\mu(Mo_{K\alpha}) = 8.520\ mm^{-1}$; 4022 measured reflections, 2010 independent reflections, 1457 with $F_o > 4\sigma(F_o)$; 118 free parameters; GOF = 1.057; R values for $F_o > 4\sigma(F_o)$: $R1 = 0.0488$, $wR2 = 0.1084$; max./min. residual electron density: $1.47/-1.55 \times 10^{-6}\ e\,pm^{-3}$. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-410869, CSD-410870, CSD-410871, and CSD-410872.

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