

Table 1. *Crystal data*

	<i>a</i>	<i>b</i>	<i>c</i>	β	Space group	<i>Z</i>	D_m^* (g.cm ⁻³)	D_x (g.cm ⁻³)
Si(O ₂ COCH ₃) ₄	7.42 ± 0.02 Å	—	11.34 ± 0.02 Å	—	<i>P</i> 4 ₂ <i>c</i>	2	1.40	1.34
Ge(O ₂ COCH ₃) ₄	7.36 ± 0.02	15.45 ± 0.03 Å	45.77 ± 0.05	—	<i>P</i> na2 ₁	16	1.43	1.51
Sn(O ₂ COCH ₃) ₄	12.93 ± 0.02	26.62 ± 0.04	7.86 ± 0.02	105.3 ± 0.2°	<i>P</i> 2 ₁	8	1.77	1.80
Pb(O ₂ COCH ₃) ₄	13.01 ± 0.02	26.59 ± 0.04	7.86 ± 0.02	105.6 ± 0.2°	<i>P</i> 2 ₁	8	2.23	2.24

* The D_m values are not accurate owing to the extremely high sensitivity of these compounds to moisture and the subsequent hydrolysis.

reflexions $0k0$ for k odd indicated $P2_1$ or $P2_1/m$ as the possible space groups for tin(IV) acetate and lead(IV) acetate. The final choice of $P2_1$ was ratified by usual statistical tests (Howells, Phillips & Rogers, 1950) and moment tests (Foster & Hargreaves, 1963).

Very close values of unit-cell parameters and the same space-group extinctions for tin(IV) acetate and lead(IV) acetate indicate isomorphism of their crystal structures.

Detailed structural investigations of the acetates of silicon, tin and lead are in progress, but we do not intend to proceed with the crystal structure analysis of germanium(IV) acetate because of its large unit cell and the diffuse reflexions at room temperature.

We thank Professor D. Grdenić for suggesting the problem and the Republic Foundation for Scientific Research, Zagreb, for financial support.

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Acta Cryst. (1972). **B28**, 322

Dehydration and transformation phases of scholzite $\text{CaZn}_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. By REINHARD CZAYA, *Mineralogisch-Petrographisches Institut und Museum der Universität Kiel, 2300 Kiel, Olshausenstrasse 40-60, Deutschland (BRD)*

(Received 17 June 1971)

Dehydration and transformation processes in scholzite from Australia have been investigated using high-temperature microscopy, thermo-gravimetric analysis, differential thermal analysis, infrared spectroscopy and single-crystal and high-temperature X-ray powder diffraction methods. The two H_2O molecules present in scholzite leave the substance without destruction of the initial single crystals at two temperatures, 188 and 402°C. The crystal structure of the monohydrate is closely related to the structure of scholzite, as deduced from single-crystal photographs, whereas the anhydride develops as a mixture of different phases (α , β and γ). Above 900°C the β -phase with hexagonal indexing ($a_0 = 5.18$, $c_0 = 7.67$ Å) alone is found. From the structural aspects of scholzite and geometrical considerations supported by high-temperature X-ray powder data an ordered trigonal double sheet $[\text{Zn}_2\text{P}_2\text{O}_8]^{2-}$ in the β -phase is proposed.

Crystals of scholzite from Australia were investigated. The crystal data are as follows: $a_0 = 17.19_1$, $b_0 = 22.52_4$, $c_0 = 6.37_1$ Å, space group $Pmcm$, $Pcm2_1$ or $P2cm$, $Z = 4$, $D_{exp} = 3.05 \pm 0.01$ g.cm⁻³. The melting point of the anhydride is $1031 \pm 2^\circ\text{C}$. Scholzite has an orthorhombic subcell with $A = a$, $B = b/3$ and $C = c/2$ (Taxer, 1970). The chemical analysis is: CaO 15.7%, ZnO 37.2%, P_2O_5 37.9%, H_2O 8.6%, and the crystals show changes in light transmission observed under the microscope at approximately 200 and 400°C. No further changes are found up to the melting point.

Differential thermal analysis (DTA) measurements indicate dehydration in two steps at 188 ± 1 and $402 \pm 1^\circ\text{C}$. Weight losses found by thermo-gravimetric analysis (TGA) measurements are 4.32% at 188°C and 4.29% at 402°C. The total weight loss of 8.61% can be attributed to the removal of two H_2O molecules (theoretical value: 8.58%). Infrared measurements (KBr method) reveal two water absorption bands at 3350 cm⁻¹ and 3420 cm⁻¹ ($3.0\mu\text{m}$ and $2.9\mu\text{m}$) for Scholzite. The monohydrate only shows the band at 3420 cm⁻¹ ($2.9\mu\text{m}$) with one half of the integral

intensity of the broad composite band found in scholzite. Single crystal X-ray photographs of the monohydrate are identical with those of scholzite but show a quadrupling of the c axis. The formation of the monohydrate is topotactic and irreversible. The anhydride also develops within the initial scholzite single crystal, as is shown in a textured X-ray photograph, and is not single-phased. At approximately 900°C the single β -phase develops from the mixture as can be seen from high-temperature powder diffraction. The β -phase can be indexed with hexagonal axes $a_0 = 5.13$, $c_0 = 7.67$ Å.

Corresponding cells have been found in the synthetic isostructural compounds $\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$ (Takeuchi & Donnay, 1959) and $\text{Ba}[\text{Al}_2\text{Si}_2\text{O}_8]$ (Takeuchi, 1958; Sorrell, 1958). Both structures are characterized by a $[\text{Al}_2\text{Si}_2\text{O}_8]^{2-}$ double-sheet which is trigonal for $\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$ and the low-temperature form of $\text{Ba}[\text{Al}_2\text{Si}_2\text{O}_8]$, whereas high-temperature form of $\text{Ba}[\text{Al}_2\text{Si}_2\text{O}_8]$ is hexagonal. For synthetic β - $\text{CaZn}_2(\text{PO}_4)_2$ the hexagonal cell with $a = 5.13$, $c = 7.67$ Å was found by Kreidler & Hummel (1966). X-ray powder

intensities taken at 900°C correspond to the values given by Kreidler & Hummel. From geometrical considerations it seems obvious that β -CaZn₂(PO₄)₂ contains a double-sheet [Zn₂P₂O₈]²⁻ with trigonal symmetry. The [Zn₂P₂O₈]²⁻ double sheet is built up from six-membered rings of tetrahedra. Each PO₄ tetrahedron is surrounded by four ZnO₄ tetrahedra and *vice versa*. The resulting symmetry of

the double sheet is trigonal. With this assumption structure-factor calculations for a model with the coordinates of Table 1 were made. This led to an *R* value of 0.29. Table 2 gives the *F_o* and *F_c* values.

The crystal structure of scholzite (Taxer, 1970) shows some characteristics which make it possible to explain the topotactic reaction mechanism which leads to trigonal double-sheets [Zn₂P₂O₈]²⁻ in the β -phase. Scholzite has layers of [Zn₂(PO₄)₂]²⁻ parallel to (100) which alternate with Ca ions and water molecules. Ca has sixfold coordination with four oxygens from different isolated PO₄ groups and two water molecules. The ZnO₄ groups form chains parallel to *c*. Its bridging oxygens at the same time link the PO₄ groups to the chain. After dehydration the *a* axis, which is normal to the [Zn₂(PO₄)₂]²⁻ layers shrinks from 17.19 to 2 × 7.67 = 15.34 Å and becomes the trigonal axis of the β -phase.

Within the [Zn₂(PO₄)₂]²⁻ sheet the Zn-O-Zn arrangement is given up as all the oxygen atoms becoming bridging oxygen atoms. The resulting trigonal unit cell of β -CaZn₂P₂O₈ with *a*₀ = 5.18 and *c*₀ = 7.67 or 2 × 7.67 Å contains one or two molecules β -Ca[Zn₂P₂O₈].

A determination of the structure of β -Ca[Zn₂P₂O₈] on the basis of high-temperature single-crystal data is planned.

The author is grateful to Professor A. Pabst, Berkeley, Dr W. Lieber, Heidelberg and Miss Rhonda Abbey, Blair Athol, Australia for supplying crystals of scholzite.

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Table 1. Coordinates of structure model for β -CaZn₂P₂O₈

Six oxygen atoms in general position *xyz* are not included.

	Equipoint of space group <i>P3</i>	<i>x</i>	<i>y</i>	<i>z</i>
Ca	1(<i>a</i>)	0	0	0
Zn(1)	1(<i>c</i>)	0.66	0.33	0.30
Zn(2)	1(<i>b</i>)	0.33	0.66	0.70
P(1)	1(<i>c</i>)	0.66	0.33	0.25
P(2)	1(<i>b</i>)	0.33	0.66	0.75
O(1)	1(<i>c</i>)	0.66	0.33	0.45
O(2)	1(<i>b</i>)	0.33	0.66	0.55

Table 2. Comparison of observed and calculated *F_{hkl}*'s corresponding to one formula unit (*F_o*, powder diffraction data at 900°C)

<i>hkl</i>	<i>F_o</i>	<i>F_c</i>
100	25.6	29.5
200	6.4	23.2
300	107.5	75.7
102	59.9	59.7
104	58.4	45.3
202	32.9	17.3
302	17.9	29.5
110	97.4	101.6
111	12.4	12.0
113	25.7	40.7
211	17.5	5.9
212	29.5	50.8

Acta Cryst. (1972). **B28**, 323

The crystal structure of bis-(γ -picoline)zinc(II) dibromide. By L. FANFANI, A. NUNZI and P. F. ZANAZZI, *Istituto di Mineralogia dell'Università di Perugia, Perugia 06100, Italy*

(Received 11 May 1971)

Zn(γ -pic)₂Br₂ is monoclinic with *a* = 14.42, *b* = 8.09, *c* = 13.89 Å, β = 101°10' and space group *P2₁/c*. The crystal structure has been solved by interpretation of the Patterson function employing three-dimensional photographic data and refined by the least-squares method to an *R* value of 0.082. The complex is tetrahedral; Zn-Br and Zn-N average distances are 2.35 and 2.05 Å respectively.

The crystal structure of ZnBr₂(γ -pic)₂ has been determined in order to collect new information on tetrahedral Zn(II) complexes. The product was obtained in an unsuccessful attempt to synthesize the tetramethylammonium salt of ZnBr₃(γ -pic)₂⁻ according to a recent preparation (Guru & Ramana Rao, 1968). The crystals of ZnBr₂(γ -pic)₂ were kindly supplied by Dr A. A. G. Tomlinson (Institute of Inorganic Chemistry of Perugia University). They are colourless, short and prismatic in habit with a density of 1.71

g.cm⁻³. The crystal data of the complex, determined by oscillation and Weissenberg photographs, are as follows: space group *P2₁/c*; *a* = 14.42 ± 0.01, *b* = 8.09 ± 0.01, *c* = 13.89 ± 0.01 Å, β = 101°10' ± 5'; *Z* = 4; *d_x* = 1.72 g.cm⁻³.

The intensity data for the structural determination were collected employing a Weissenberg equi-inclination technique using Cu *K* α radiation. Diffraction effects of the reciprocal lattice layers from *h0l* to *h6l* were recorded and measured with a microdensitometer. Absorption correction