intensities taken at 900°C correspond to the values given by Kreidler & Hummel. From geometrical considerations it seems obvious that β-$CaZn_2(PO_4)_2$ contains a double-sheet $[Zn_2P_2O_8]^{2-}$ with trigonal symmetry. The $[Zn_2P_2O_8]^{2-}$ double sheet is built up from six-membered rings of tetrahedra. Each PO_4 tetrahedron is surrounded by four ZnO_4 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.

Table 1. *Coordinates of structure model for* β-$CaZn_2P_2O_8$

Six oxygen atoms in general position xyz are not included.

	Equipoint of space group $P3$	x	y	z
Ca	1(*a*)	0	0	0
Zn(1)	1(*c*)	0·66	0·33	0·30
Zn(2)	1(*b*)	0·33	0·66	0·70
P(1)	1(*c*)	0·66	0·33	0·25
P(2)	1(*b*)	0·33	0·66	0·75
O(1)	1(*c*)	0·66	0·33	0·45
O(2)	1(*b*)	0·33	0·66	0·55

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

hkl	F_o	F_c
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

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 $[Zn_2P_2O_8]^{2-}$ in the β-phase. Scholzite has layers of $[Zn_2(PO_4)_2]^{2-}$ parallel to (100) which alternate with Ca ions and water molecules. Ca has sixfold coordination with four oxygens from different isolated PO_4 groups and two water molecules. The ZnO_4 groups form chains parallel to **c**. Its bridging oxygens at the same time link the PO_4 groups to the chain. After dehydration the a axis, which is normal to the $[Zn_2(PO_4)_2]^{-2}$ layers shrinks from 17·19 to $2\times7{\cdot}67=15{\cdot}34$ Å and becomes the trigonal axis of the β-phase.

$$\begin{array}{c} \mathrm{P} \\ | \end{array}$$

Within the $[Zn_2(PO_4)_2]^{2-}$ 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-$CaZn_2P_2O_8$ with $a_o=5{\cdot}18$ and $c_o=7{\cdot}67$ or $2\times7{\cdot}67$ Å contains one or two molecules β-$Ca[Zn_2P_2O_8]$.

A determination of the structure of β-$Ca[Zn_2P_2O_8]$ 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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The crystal structure of bis-(γ-picoline)zinc(II) dibromide.

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(*Received* 11 *May* 1971)

$Zn(\gamma\text{-pic})_2Br_2$ is monoclinic with $a=14{\cdot}42$, $b=8{\cdot}09$, $c=13{\cdot}89$ Å, $\beta=101°10'$ and space group $P2_1/c$. 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 $ZnBr_2(\gamma\text{-pic})_2$ 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 $ZnBr_3(\gamma\text{-pic})_2^-$ according to a recent preparation (Guru & Ramana Rao, 1968). The crystals of $ZnBr_2(\gamma\text{-pic})_2$ 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 $P2_1/c$; $a=14{\cdot}42\pm0{\cdot}01$, $b=8{\cdot}09\pm0{\cdot}01$, $c=13{\cdot}89\pm0{\cdot}01$ Å, $\beta=101°10'\pm5'$; $Z=4$; $d_x=1{\cdot}72$ g.cm^{-3}.

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

($\mu = 86{\cdot}7$ cm^{-1} for Cu $K\alpha$; crystal dimensions: $0{\cdot}07 \times 0{\cdot}08 \times 0{\cdot}11$ mm) was applied using the program of De Meulenaer & Tompa (1965). After the geometrical corrections the squared amplitudes were put on approximately the same relative scale by means of the common data on the $0kl$ layer.

About 2000 independent reflexions were obtained, of which 735 were in the measurable range.

From a three-dimensional Patterson function the Zn, Br(1) and Br(2) atoms were easily located. The coordinates of the atoms of the two picoline rings were determined by a Fourier synthesis computed with the signs given by the heavier atoms. The refinement of the structure was performed by the least-squares method, employing a block-diagonal program written by Shiono for the IBM 1130 computer. After four cycles with isotropic individual thermal factors, a last cycle was computed varying the temperature factors of Zn and Br atoms, anisotropically; the R index reached the final value 0·082. The data were weighted using Hughes's (1941) scheme. Observed and calculated structure factors are compared in Table 1. The atomic coordinates and temperature factors are given in Table 2. The scattering factors used in the calculations for Br, Zn, N, and C were obtained from *International Tables for X-ray Crystallography* (1962).

Bond lengths and angles around the Zn^{2+} ion are listed with their estimated standard deviations in Table 3. The structure projected along the b axis is represented in Fig. 1. The complex is distorted tetrahedral; Zn–Br distances, 2·35 Å, are in agreement with those reported by MacGillavry & Bijvoet (1936) for $Zn(NH_3)_2Br_2$, 2·38 Å. The Zn–N distances (2·07 and 2·03 Å) are comparable with those found in bis(imidazole)zinc(II) dichloride (Lundberg, 1966) and in bis(pyridine)zinc(II) dichloride (Sokolova, Atovmyan & Poray-Koshits, 1966), (2·01 Å on average). The tetrahedral distortion may be caused by steric hindrance between the

Table 1. *Observed and calculated structure factors* ($\times 10$) *of reflexions with intensities in the measurable range*

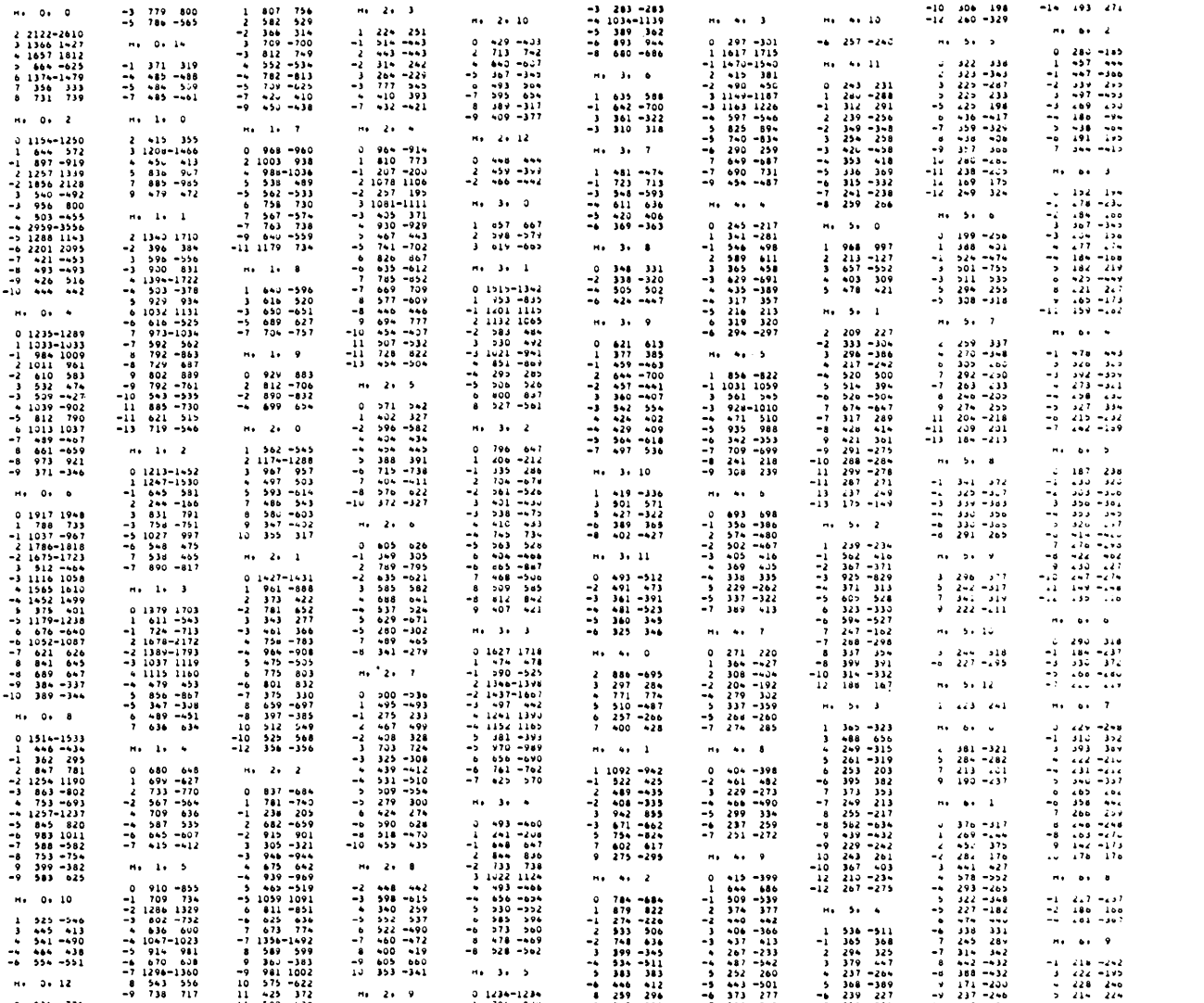

Table 2. *Fractional atomic coordinates* ($\times 10^4$) *and thermal parameters with relative standard deviations*

	x/a	*y/b*	*z/c*	*B*(Å)^2
Zn	7535 (4)	1970 (7)	1894 (4)	*
Br(1)	7075 (4)	4757 (6)	1734 (4)	*
Br(2)	7572 (4)	541 (7)	3376 (4)	*
N(1)	8857 (21)	1864 (35)	1530 (21)	3·2 (0·6)
N(2)	6743 (22)	677 (35)	775 (22)	2·7 (0·6)
C(1)	9524 (27)	801 (43)	2027 (28)	3·5 (0·8)
C(2)	10420 (27)	627 (45)	1740 (27)	4·1 (0·8)
C(3)	10568 (29)	1525 (44)	898 (27)	3·5 (0·8)
C(4)	9907 (27)	2631 (44)	390 (27)	3·5 (0·8)
C(5)	9054 (27)	2698 (46)	803 (27)	3·6 (0·8)
C(6)	11473 (28)	1312 (46)	605 (27)	3·9 (0·8)
C(7)	6433 (29)	1457 (44)	−131 (27)	2·7 (0·8)
C(8)	5936 (27)	548 (46)	−940 (30)	3·6 (0·8)
C(9)	5820 (28)	−1006 (45)	−892 (28)	3·4 (0·8)
C(10)	6132 (29)	−1826 (44)	6 (27)	3·4 (0·8)
C(11)	6616 (27)	−947 (44)	832 (28)	2·9 (0·8)
C(12)	5362 (26)	−2166 (47)	−1787 (26)	3·3 (0·8)

* The anisotropic temperature factors of Zn, Br(1) and Br(2), given in the form $T=\exp\{-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\times 10^{-4}\}$ are as follows:

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	66 (4)	166 (11)	79 (4)	12 (6)	12 (3)	3 (5)
Br(1)	89 (4)	240 (10)	60 (4)	14 (5)	16 (3)	10 (5)
Br(2)	54 (4)	186 (11)	59 (4)	8 (5)	7 (3)	3 (5)

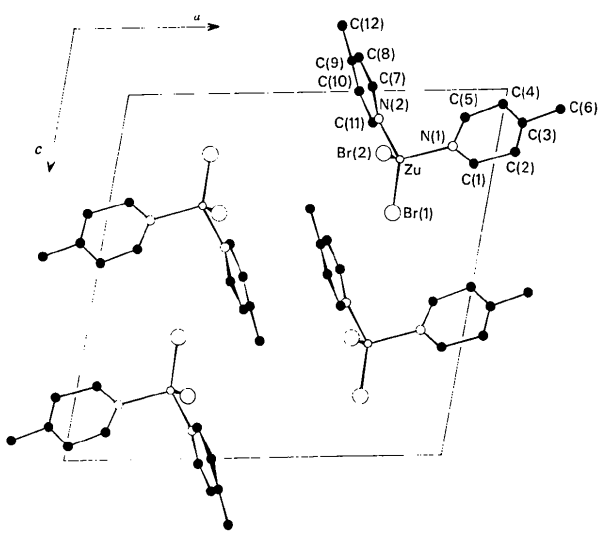

Fig. 1. Projection of the structure along the *b* axis.

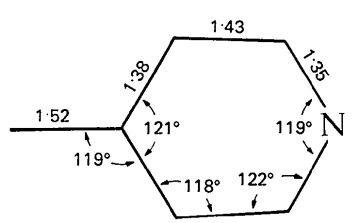

Fig. 2. Sketch of the ligand with averaged bond lengths and angles.

two bromine atoms: the angle Br(1)–Zn–Br(2) is 120·9°; the Br–Br distance in the complex is 4·09 Å.

Table 3. *Distances and angles around* Zn *with their standard deviations*

Zn–Br(1)	2·35	±0·01 Å
Zn–Br(2)	2·35	0·01
Zn–N(1)	2·07	0·03
Zn–N(2)	2·03	0·03
Br(1)–Zn–Br(2)	120·9°	±0·3°
Br(1)–Zn–N(1)	105·9	0·9
Br(1)–Zn–N(2)	108·3	0·9
Br(2)–Zn–N(1)	109·1	0·9
Br(2)–Zn–N(2)	109·3	0·9
N(1)–Zn–N(2)	101·6	1·3

Individual bond lengths and angles in the picoline rings are not reported in detail because they have poor significance for the high standard deviations (σ_{C-C} and σ_{C-N}= 0·05 Å). However a sketch of the ligand with the averaged values of equivalent bond lengths and angles in the two molecules is reported in Fig. 2. The rings are planar within experimental error, the least-square plane equations computed for the six atoms of the heterocyclic ring being:

$0{\cdot}682\,x+1{\cdot}038\,y+1{\cdot}311\,z=1$ for the ring containing N(1) and

$1{\cdot}581\,x-0{\cdot}166\,y-0{\cdot}728\,z=1$ for that containing N(2).

The interplanar angle is 77°15′. The central Zn^{2+} ion is out of both the mean square planes with deviations of about 0·18 Å. The carbon atoms of the methyl groups, C(6) and C(12), deviate by 0·01 Å and 0·12 Å respectively from the planes of relative rings.

Table 4. *Shortest intermolecular contacts*

(*a*) $2-x, \frac{1}{2}+y, \frac{1}{2}-z$ (*d*) $2-x, -\frac{1}{2}+y, \frac{1}{2}-z$
(*b*) $x, \frac{1}{2}-y, \frac{1}{2}+z$ (*e*) $2-x, -y, -z$
(*c*) $x, 1+y, z$ (*f*) $1-x, -y, -z$

Br(1)–C(2) (*a*)	3·86 Å	Br(2)–C(5) (*b*)	3·90 Å
Br(1)–C(8) (*b*)	3·92	Br(2)–C(7) (*b*)	3·77
Br(1)–C(10) (*c*)	3·75	Br(2)–C(6) (*d*)	3·85
Br(1)–C(11) (*c*)	3·72		
C(3)–C(3) (*e*)	3·67 Å	C(7)–C(10) (*f*)	3·61 Å
		C(7)–C(11) (*f*)	3·70

The shortest intermolecular contacts are given in Table 4.

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