# The crystal structure of RbZn₁₃. By GIACOMO BRUZZONE, *Institute of Physical Chemistry, Genoa University, Genoa, Italy*

The occurrence of intermetallic compounds on the 1:13 stoichiometric ratio was investigated for the following binary systems: Ba–Be, Rb–Zn and Cs–Zn. The existence of the $RbZn_{13}$ phase, isomorphous with $NaZn_{13}$ ($D2_3$), was recognized ($a_0 = 12 \cdot 420 \pm 0 \cdot 003$ Å). Observed $d$ spacings and intensities are reported together the calculated values. The interatomic distances are briefly examined in order to evaluate the influence of the atomic sizes on the stability of the structure.

The crystal structure of the known $MX_{13}$ intermetallic phases belongs to the cubic $NaZn_{13}$ ($D2_3$) type.

In this structure each $Zn_I$ atom is surrounded by 12 $Zn_{II}$ atoms at the vertices of a nearly regular icosahedron and each Na atom by 24 $Zn_{II}$ at the vertices of a nearly regular snub cube. By this atomic arrangement, Sanderson & Baenziger (1953) pointed out that the occurrence of these $MX_{13}$ intermetallic phases would largely depend on the 'size factor', the sub-lattice of the X component determining the radius of the hole where an M atom lies, so that the structure cannot be stable for too large (or small) M atoms. In this way they explained that Ca for the $MBe_{13}$ phases, K for the $MZn_{13}$ phases, and Cs for the $MCd_{13}$ phases were the biggest M components.

However, the existence of the $SrBe_{13}$ compound was reported afterwards (Matjušenko, Verkhorobin & Karev, 1964); therefore, the examination of other cases with very large M atoms appeared of some interest. To this purpose the $RbZn_{13}$, $CsZn_{13}$ and $BaBe_{13}$ compositions were examined.

Metals of good purity were used [Ba 99·8 % wt, Rb and Cs 99·98%, Be 99·9% wt and Zn 99·999% wt]. The Zn alloys were prepared by placing stoichiometric quantities of the two components in Pyrex tubes under a low pressure atmosphere of very pure argon and heating to 400°C. Brittle ingots, which oxidize in the air, were obtained. The walls of the Pyrex containers were unattacked by the alloys.

The formation of a Ba–Be compound was investigated by several other methods, but no reaction between the two metals was observed. For the Rb–Zn and Cs–Zn systems evidence of an intermediate phase was found: in the case of Cs the crystal structure of the compound does not correspond to the $NaZn_{13}$ type and its composition and structure is to be investigated; in the case of Rb the existence of the cubic $RbZn_{13}$ compound, isomorphous with $NaZn_{13}$, was recognized. The lattice constant is $a_0 = 12 \cdot 420$ ($\pm 0 \cdot 003$) Å. The diffraction patterns of powder specimens were taken with iron $K\alpha$ radiation using a Debye camera of diameter 114·6 mm.

The intensities of the reflexions were calculated for different values of the $y$ and $z$ atomic parameters in the following respective ranges: $0 \cdot 178 \leq y \leq 0 \cdot 185$; $0 \cdot 115 \leq z \leq 0 \cdot 120$.

The set of values which gives the best agreement with the observed intensities coincides with that reported by Shoemaker, Marsh, Ewing & Pauling (1952) for $NaZn_{13}$: $y = 0 \cdot 180$ and $z = 0 \cdot 119$. The final calculated intensities are reported in Table 1 in comparison with the observed ones, which were visually estimated. Calculated and observed values of the $d$-lattice spacings are also collected in Table 1.

The interatomic distances, reported in Table 2, show that the distance from $Zn_I$ to each of the 12 $Zn_{II}$ (2·683 Å) is slightly greater than that known for the 6 shorter ligates in

the elementary metal (2·660 Å), while the smallest $Zn_{II}$–$Zn_{II}$ distance (2·608 Å) corresponds to some contraction.

Table 1. *X-ray powder data for* RbZn₁₃

(NaZn₁₃ type structure; $a_0 = 12 \cdot 420 \pm 0 \cdot 003$ Å)

| hkl | $d_{obs}$ | $d_{calc}$ | $I_{calc}$ | $I_{obs}$ |
|---|---|---|---|---|
| 420 | 2·7755 | 2·7772 | 15·0 | $w^+$ |
| 422 | 2·5345 | 2·5352 | 45·0 | ms |
| 440 | — | 2·1956 | 2·7 | — |
| 531 | 2·0985 | 2·0994 | 100·0 | vs |
| 600+442 | 2·0689 | 2·0700 | 31·5 | m |
| 620 | 1·9630 | 1·9638 | 12·6 | w |
| 622 | — | 1·8724 | 0·2 | — |
| 444 | 1·7920 | 1·7927 | 9·1 | vw |
| 640 | 1·7213 | 1·7223 | 11·2 | w |
| 642 | 1·6588 | 1·6597 | 12·5 | w |
| 731 | — | 1·6169 | 1·1 | — |
| 800 | 1·5523 | 1·5525 | 11·4 | w |
| 820+644 | 1·5055 | 1·5061 | 16·8 | $w^+$ |
| 822+660 | 1·4640 | 1·4637 | 9·4 | vw |
| 751+662 | 1·4345 | 1·4341 | 6·2 | vvw |
| 840 | — | 1·3886 | 2·2 | — |
| 753 | 1·3630 | 1·3633 | 39·5 | ms |
| 842 | — | 1·3551 | 2·4 | — |
| 664 | 1·3235 | 1·3240 | 3·4 | vvw |
| 931 | 1·3025 | 1·3020 | 27·5 | $m^-$ |
| 844 | 1·2675 | 1·2676 | 38·8 | m |
| 10·00+860 | 1·2420 | 1·2420 | 38·7 | m |
| 10·20+862 | 1·2180 | 1·2179 | 32·2 | m |
| 951 | 1·2008 | 1·2007 | 28·8 | $m^-$ |
| 10·22+666 | — | 1·1951 | 4·9 | — |
| 953 | 1·1583 | 1·1582 | 80·9 | s |
| 864+10·40 | 1·1532 | 1·1532 | 12·8 | w |
| 10·42 | 1·1336 | 1·1338 | 15·8 | $w^+$ |
| 880 | — | 1·0978 | 1·1 | — |
| 11·31+971 | 1·0853 | 1·0851 | 77·2 | ms–s |
| 10·44+882 | 1·0816 | 1·0810 | 80·5 | s |
| 10·60+866 | 1·0652 | 1·0650 | 65·2 | ms–s |
| 973 | 1·0537 | 1·0535 | 21·8 | m–w |
| 10·62 | — | 1·0497 | 0·2 | — |
| 12·00+884 | 1·0350 | 1·0350 | 22·4 | m–w |

(vw = very weak; ms = medium strong)

Table 2. *Interatomic distances in* RbZn₁₃

| Type of distance | n | D(Å) |
|---|---|---|
| $Zn_I(0,0,0) - Zn_{II}(0,y,z)$ | 12 | 2·683 |
| $Zn_{II}(0,y,z) - Zn_{II}(0,z,\frac{1}{2}-y)$ | 2 | 2·608 |
| $- Zn_I(0,0,0)$ | 1 | 2·683 |
| $- Zn_{II}(z,\frac{1}{2}-y,0)$ | 2 | 2·720 |
| $- Zn_{II}(z,0,y)$ | 4 | 2·782 |
| $- Zn_{II}(0,y,\bar{z})$ | 1 | 2·956 |
| $- Rb(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ | 2 | 3·615 |
| $Rb(\frac{1}{4},\frac{1}{4},\frac{1}{4}) - Zn_{II}(0,y,z)$ | 24 | 3·615 |

From the Rb–Zn distance value (3·615 Å) a contraction greater than 10% in the atomic radius of Rb metal can be evaluated. This fact and the expansion of part of the Zn bonds indicate that the stability of this type of structure is actually coming down, although the existence of $RbZn_{13}$ is beyond the suggestion of Sanderson & Baenziger (1953).

**References**

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# The crystallography of nitramine–solvent complexes. I. Crystallographic data on 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (BSX) and on its complexes with acetone, nitromethane, acetonitrile and acetophenone.

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Pure BSX crystallizes from acetone at room temperature in tablets, space group C2, Cm or C2/m with $a=26\cdot24$, $b=9\cdot17$, $c=6\cdot14$ Å, $\beta=91\cdot5°$, $Z=4$. At 0°C acicular crystals in $P2_1/n$ are obtained with $a=14\cdot54$, $b=20\cdot47$, $c=6\cdot38$ Å, $\beta=91\cdot5°$. Similar acicular crystals are obtained from the three other solvents. Those from acetone, nitromethane and acetonitrile appear to be 1:1 solvent/BSX complexes, from acetophenone 1:2 solvent/BSX. Optical data are given.

This paper describes the results of investigations carried out some time ago, elsewhere, which have not been previously published; it is presented now because of current interest in these complexes (Hall, 1970) and to serve as an introduction to some later papers describing the structure determination of some complexes of this type.

1,7-Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane, which has the trivial name BSX, may be crystallized from acetone at room temperature to give flat monoclinic crystals tabular on {100} and showing the forms {110} and {011}. The cell dimensions and space group of these crystals were determined by means of oscillation photographs using Cu Kα ($\lambda=1\cdot5418$ Å) radiation; these data and the crystal density are given in Table 1.

Table 1. *Crystallographic data for pure BSX (tabular crystals)*

$a=26\cdot24$ (2) Å*  Space group C2 or Cm or C2/m
$b=\ 9\cdot17$ (1) Å  Density: observed 1·590 (4)
$c=\ 6\cdot14$ (1) Å  calculated 1·592, for four
$\beta=91\cdot5$ (2)°  molecules of $C_8H_{14}N_6O_{10}$
($M=354$).

\* Figures in parenthesis show the standard deviation in the last figure.

Crystallization of BSX from acetone at 0° gave monoclinic crystals acicular along [c] and exhibiting the forms {010}, {110} and {101}. These crystals were observed to transform to normal tabular BSX if the temperature was raised to 15°C while they were in contact with saturated solution. When in the dry condition at 15°C the crystals gradually became opaque (pseudomorphic) and suffered a weight loss corresponding to one molecule of acetone per molecule of BSX. Similar acicular crystals were grown from nitromethane and acetonitrile at 0°C and from acetophenone at 25°C. Other solvents including ethyl acetate and ethylidene chloride yielded crystals of normal tabular BSX at 0°C. The acicular crystals from different solvents were found to have similar cell dimensions and the same space group. Agreement between the density calculated from the cell dimensions and the observed density could only be obtained on the assumption of a molecular weight based on a 1:1 solvent/BSX complex in the case of the crystals grown from acetone, nitromethane and acetonitrile and a 1:2 solvent/BSX complex for the crystals from acetophenone. The results are summarized in Table 2. It was noted that the space group $P2_1/n$ is incompatible with an ordered structure containing two molecules of acetophenone per unit cell.

Table 2. *Crystallographic data for the acicular crystals*

| Solvent | Acetone | Nitromethane | Acetonitrile | Acetophenone |
|---|---|---|---|---|
| $a$ (Å) | 14·54 (1) | 14·23 (1) | 14·15 (1) | 14·40 (1) |
| $b$ (Å) | 20·47 (2) | 20·24 (2) | 20·01 (2) | 20·05 (2) |
| $c$ (Å) | 6·38 (1) | 6·38 (1) | 6·31 (1) | 6·38 (1) |
| $\beta$ (°) | 91·5 (2) | 92·5 (2) | 93·5 (2) | 92·5 (2) |
| Space group | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ |
| Density observed (g.ml$^{-3}$) | 1·418 (4) | 1·519 (4) | 1·454 (4) | 1·482 (4) |
| Molecular weight (assumed) | 412 | 415 | 395 | 414 |
| Density, calculated (g.ml$^{-3}$) | 1·441 | 1·501 | 1·471 | 1·494 |