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On the Crystal Structure of $Na_2H_2GeO_4(H_2O)_6$

EVA-BRITT BAURÉN and NILS INGRI*

Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm 70, Sweden

An X-ray investigation of the crystal structure of $Na_2H_2GeO_4(H_2O)_6$ has been started. The crystals are monoclinic ($a = 6.57 \pm 0.05$ Å, $b = 17.89 \pm 0.03$ Å, $c = 8.47 \pm 0.05$ Å, $\beta = 91.0° \pm 0.5°$) and belong to space group No. 14, $P2_1/c$. The positions of the 4 germanium atoms in the unit cell have been determined. The positions of the sodium and oxygen atoms will be given in a forthcoming publication.

Crystals of $Na_2H_2GeO_4(H_2O)_6$ have been studied previously with X-ray methods by Nowotny and Szekely.[1] Weissenberg and powder photographs indicated an orthorhombic unit cell with the dimensions: $a = 6.51$ kX, $b = 17.34$ kX, $c = 8.42$ kX. From the Weissenberg photographs $hk0$, $h0l$ and $0kl$ they[1,2] proposed that the crystals belong to space group No. 51, *Pmma*. From dehydration studies of the crystals they found that the formula $Na_2H_2GeO_4(H_2O)_6$ was more probable than $Na_2GeO_3(H_2O)_7$.

In order to determine the Ge—O coordination in $Na_2H_2GeO_4(H_2O)_6$, we decided to make a complete structure determination of the crystals. There are good reasons[3] to assume that the crystals are built up of isolated, mononuclear germanate ions. By pursuing this investigation we hope to find out whether these are tetrahedral $GeO_2(OH)_2^{2-}$ ions or octahedral $Ge(OH)_6^{2-}$ ions, which may give valuable aid in proposing reasonable formula for germanate species found in aqueous solution.[3]

PREPARATION OF THE CRYSTALS

The crystals were synthesized in the following way: 0.818 g of sodium hydroxide were molten with 0.531 g of GeO_2 in a platinum vessel. The melt was soaked with water. The sodium germanate solution obtained was collected in a plastic vessel and placed for crystallization in a desiccator with sulfuric acid. After one or two days plate-like or needle-like, very hygroscopic crystals were obtained. The plates were elongated hexagons. The needles crystallized in groups like stars. The form of the crystals was in agreement with the description given by Nowotny and Szekely.[1]

The *average charge* of the germanate ion was determined by adding a known amount of $Na_2H_2GeO_4(H_2O)_6$ to an excess of standardized perchloric acid. Then the excess of hydrogen ions was titrated with sodium hydroxide by using a glass electrode. The equivalence point, determined from a Gran plot,[10] gave an average charge per Ge of -1.94 compared with -2.0 calculated for $Na_2H_2GeO_4(H_2O)_6$.

* Present address: Department of Inorganic Chemistry, University of Umeå, Umeå 6, Sweden.

The *water content* of the crystals was determined according to Penfield [4] and according to Karl Fischer.[5] However, no good agreement between different determinations was obtained and the values of the water analysis varied between 36.4 % and 36.9 %, which may be due to the fact that the crystals are very hygroscopic. The calculated value for $Na_2H_2GeO_4(H_2O)_6$ is 43.0 % and for $Na_2H_2GeO_4(H_2O)_5$ 39.36 %.

The density was determined in a mixture of bromobenzene and tetrabromomethane with the flotation method and a value of 2.05 g/ml was obtained.

X-RAY DIFFRACTION DATA

Single crystals were selected and rotational (around [001], [100] and [010]) and Weissenberg photographs (*hk*0—*hk*4, 0*kl*—3*kl*, *h*0*l*—*h*8*l*) were taken using Cu$K\alpha$ radiation and the multiple film technique. The crystals were kept in a sealed capillary of lithium borate glass. The powder photographs were taken in a Guinier focusing camera using Cu$K\alpha$-radiation and KCl as internal standard ($a_{KCl} = 6.29294$ Å at 22°C [6]). The following cell dimensions were calculated.

$a = 6.57 \pm 0.05$ Å, $b = 17.89 \pm 0.03$ Å, $c = 8.47 \pm 0.04$ Å, $\beta = 91.0 \pm 0.5°$, $V = 995.3$ Å^3.

In Table 1 observed and calculated $\sin^2\theta$ are given.

The unit cell contains four formula units $Na_2H_2GeO_4(H_2O)_6$ giving a calculated density of 1.95 g/ml as compared with our observed value of 2.05 g/ml.

Reflections systematically absent are:

*h*0*l* with *l* odd
0*k*0 with *k* odd

This is characteristic for space group No. 14, $P2_1/c$, in the *International Tables*.[7]

The symmetry we have obtained for $Na_2H_2GeO_4(H_2O)_6$ is different from that proposed by Nowotny and Szekely.[1] From the fact that these authors used only the Weissenberg photographs *hk*0, *h*0*l* and 0*kl* and that β is very close to 90° it cannot be excluded that our crystals and theirs may be equivalent. However, the crystals prepared by us could also be another form of $Na_2H_2GeO_4(H_2O)_7$ than those prepared by Nowotny and Szekely.[1,2]

THE POSITIONS OF THE GERMANIUM ATOMS

For the determination of the germanium parameters we calculated the projections *P*(*pvw*) and *P*(*upw*) (see Fig. 1). For this calculation, the intensities were estimated visually using an intensity scale and corrected for polarization and Lorentz' effects. No correction was applied for the absorption.

In space group No. 14, $P2_1/c$, atoms may be situated in 2-fold (2(*a*), 2(*b*), 2(*c*) and 2(*d*)) or 4-fold (4(*e*)) positions. Since there are four germanium atoms in the unit cell they must be situated either in two 2-fold positions or in one 4-fold position. All combinations involving 2-fold positions can, however, be excluded as there is no peak in *P*(*pvw*) corresponding to the interatomic vector ($\frac{1}{2}\frac{1}{2}$). Therefore, only the 4-fold position need to be considered.

Table 1. Powder data of $Na_2H_2GeO_4(H_2O)_6$. Guinier camera, Cu$K\alpha$ radiation. KCl as internal standard.

hkl	$10^4\sin^2\theta$ calc	$10^4\sin^2\theta$ obs	I_{obs}	*hkl*	$10^4\sin^2\theta$ calc	$10^4\sin^2\theta$ obs	I_{obs}
		197	vw	150	6019		
020	743	769	w	220	6252		
011	1014	1030	m	042	6285	6278	m
100	1408	1377	vvw	132	6288		
110	1563	1617	st	211	6449	6598	w
021	1571			060	6685	6654	w
120	2120	2185	vvw	151	6811	6879	w
111	2354	2382	w	221	7006	6977	vw
031	2500	2523	w	230	7180		
121	2911	2968	st	061	7513	7434	vw
040	2971			042	7588		
040	2971	3109?	vst	013	7643	7738	w
130	3048			231	7934		
130	3048	3163?	vst	052	7957		
002	3305	3453	vst	160	8062		
012	3500	3546	vw	023	8200	8351	st
014	3800	3940	vvw	240	8480	8413	st
131	3840			202	8674	8787	w
022	4057	4139	vvw	161	8853		
104	4348	4242	vst	212	8860	8970	w
102	4617	4647	m	113	8909		
112	4803	4837	vvw	033	9129		
032	4986	4939	vvw	241	9234	9178	vvw
141	5139	5108	m	152	9259		
122	5360	5305	m	222	9417	9504	m
051	5471	5445	m	123	9466	9625	vvw
200	5509	5681	m				
210	5694						

We may thus start the analysis of the Patterson functions shown in Fig. 1 by assuming the four germanium atoms to be situated in the following point position:

$$4 \text{ Ge in } 4(e): \pm (xyz); \pm (\bar{x}, \tfrac{1}{2}+y, \tfrac{1}{2}-z);$$

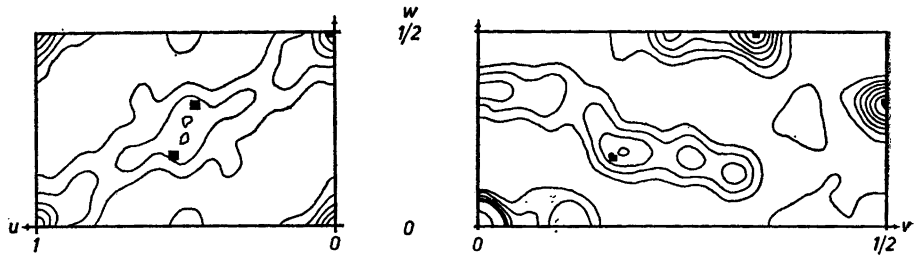

Fig. 1. Patterson projections $P(upw)$ and $P(pvw)$ for $Na_2H_2GeO_4(H_2O)_6$. The vectors Ge—Ge have been marked out. In the peak at 0.0 in $P(pvw)$ some contours have been left out.

In the Patterson space $P(uvw)$ these points will give rise to maxima corresponding to the following Ge—Ge vectors:

$$\pm (2x, \pm 2y, 2z); \pm (2x, \tfrac{1}{2}, 2z + \tfrac{1}{2}); \pm (0, \tfrac{1}{2} + 2y, \tfrac{1}{2}).$$

The Patterson projection $P(pvw)$, given in Fig. 1, shows (besides the maximum at the origin) two large maxima: one at $v = \frac{1}{2}$, $w = 0.311_2$ and one at $v = 0.339_5$, $w = \frac{1}{2}$. These maxima certainly correspond to the Ge—Ge vectors $\pm(\frac{1}{2}, 2z + \frac{1}{2})$ and $\pm(2y + \frac{1}{2}, \frac{1}{2})$. Since the space considered for the germanium parameters can be restricted to $0 \leq x \leq \frac{1}{2}$, $0 \leq y \leq \frac{1}{4}$, $0 \leq z \leq \frac{1}{4}$ we get $y = 0.080_3$ and $z = 0.094_4$ from these vectors.

In $P(upw)$, given in Fig. 1, there is a broad maximum at $u \approx 0.50, w \approx 0.25$ which is probably composed of two peaks, one at $u = 0.507$, $w = 0.221$ and one at $u = 0.493$, $w = 0.279$. They should correspond to the vectors $\pm$ $(2x,2z)$, $\pm$ $(2x, 2z-\frac{1}{2})$, and we get $x \approx 0.250$ and $z = 0.125$. However, because of the overlapping of the peaks in $P(upw)$, the values for x and z could not be considered to be very accurate.

In $P(uvp)$, given in Fig. 1 we found three high peaks (they were approximately three times as high as all other peaks in the projection) at $u = 0.5000$, $v = 0.155_0$, at $u = 0$, $v = 0.342_5$, and at $u = 0.500_0$, $v = \frac{1}{2}$. They should correspond to the vectors $\pm(2x, \pm 2y)$; $\pm(0, 2y \pm \frac{1}{2})$, which give $x = 0.250_0$ and $y = 0.078_1$.

The following positions are thus proposed for the germanium atoms in the unit cell:

$$4 \text{ Ge in } 4(e) \text{ with } x = 0.250_0,\ y = 0.079_2,\ z = 0.094_4$$

The germanium contributions to the intensities were calculated with these parameters and, even though the oxygen and sodium contributions were not included, a rather good agreement between observed and calculated intensities was obtained.

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