Table 1.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x \pm \sigma_x$</th>
<th>$y \pm \sigma_y$</th>
<th>$z \pm \sigma_z$</th>
<th>$B \pm \sigma_B$ Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi₁</td>
<td>0.88945 ± 0.00016</td>
<td>0.10690 ± 0.00018</td>
<td>0.24595 ± 0.00019</td>
<td>1.711 ± 0.019</td>
</tr>
<tr>
<td>N₁</td>
<td>0.38748 ± 0.00458</td>
<td>0.11343 ± 0.00501</td>
<td>0.26855 ± 0.00571</td>
<td>2.277 ± 0.584</td>
</tr>
<tr>
<td>F₁</td>
<td>0.08350 ± 0.00306</td>
<td>0.14232 ± 0.00336</td>
<td>0.54453 ± 0.00388</td>
<td>2.100 ± 0.365</td>
</tr>
<tr>
<td>F₂</td>
<td>0.72081 ± 0.00309</td>
<td>0.17982 ± 0.00349</td>
<td>0.49744 ± 0.00376</td>
<td>2.297 ± 0.380</td>
</tr>
<tr>
<td>F₃</td>
<td>0.90583 ± 0.00245</td>
<td>0.07342 ± 0.00268</td>
<td>0.87537 ± 0.00306</td>
<td>1.229 ± 0.264</td>
</tr>
<tr>
<td>F₄</td>
<td>0.32291 ± 0.00365</td>
<td>0.04674 ± 0.00404</td>
<td>0.85739 ± 0.00444</td>
<td>2.864 ± 0.448</td>
</tr>
</tbody>
</table>

The Crystal Structure of Bi₂GeO₅.

BENGT AURIVILLIUS, CLAES-IVAR LINDBLOM and PER STENSON

Institutes of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

The investigation of the crystal structures of Bi₂GeO₅ and Bi₂SiO₅ is a part of the more general study of the coordination of bismuth in compounds containing tetrahedral anions.

The compounds were synthesized by heating a mixture of the corresponding oxides in the molecular proportions 1:1 in platinum crucibles, immersed in a series of porcelain crucibles in an electrical furnace. The temperature was slowly increased to ~1000°C. After 2 or 3 h at that temperature, the samples were cooled down very slowly. This mode of preparation explains why previous investigators of the systems Bi₂O₃-GeO₂ and Bi₂O₃-SiO₂ have not reported these phases.

Single crystals of Bi₂GeO₅ were investigated by X-ray single crystal diffraction methods. The intensity material was made up of 272 independent reflections. The intensities were corrected for absorption. The unit-cell dimensions of the compounds were determined from X-ray Guinier diagrams.

The following data were derived for the compounds:

Space group: Cmc2₁ (No. 36).
8 Bi, 8 O₅, and 8 O₂ in 8(8):
$$(0,0,0;\frac{1}{4},\frac{1}{4},0) + x,y,z; \bar{x},\bar{y},\bar{z} + z;$$
$$x,y,\frac{1}{4} + z.$$
4 Ge (Si) and 4 O₁ in 4(a):
$$(0,0,0;\frac{1}{4},\frac{1}{4},0) + 0,y,z; 0,\bar{y},\frac{1}{4} + z.$$
Table 1.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x \pm \sigma_x$</th>
<th>$y \pm \sigma_y$</th>
<th>$z \pm \sigma_z$</th>
<th>$B \pm \sigma_B \text{Å}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>0.16758 ± 0.00013</td>
<td>0.21738 ± 0.00043</td>
<td>0.25000</td>
<td>1.192 ± 0.042</td>
</tr>
<tr>
<td>Ge</td>
<td>0</td>
<td>0.68572 ± 0.00209</td>
<td>0.20003 ± 0.00219</td>
<td>1.083 ± 0.188</td>
</tr>
<tr>
<td>O₁</td>
<td>0</td>
<td>0.5803 ± 0.0161</td>
<td>0.4908 ± 0.0197</td>
<td>1.98 ± 1.47</td>
</tr>
<tr>
<td>O₂</td>
<td>0.0949 ± 0.0026</td>
<td>0.1368 ± 0.0085</td>
<td>0.6482 ± 0.0108</td>
<td>0.35 ± 0.64</td>
</tr>
<tr>
<td>O₃</td>
<td>0.2541 ± 0.0021</td>
<td>0.4777 ± 0.0079</td>
<td>0.4621 ± 0.0104</td>
<td>0.44 ± 0.70</td>
</tr>
</tbody>
</table>

Fig. 1. Perspective view of the content of one unit cell of Bi₂GeO₅ from $x = 0$ to $x = 0.33$, showing the deformed Bi₂O₅⁺⁺ layers and the GeO₅⁻⁻ chains. Notations: Bi □; Ge ●; O ○. The Bi atoms are connected by full lines with their closest oxygen atom neighbours in the Bi₂O₅⁺⁺ layer. The linked GeO₅ tetrahedra are also shown by full lines. The axes correspond to the crystallographic ones.

Unit-cell dimensions: Bi₂GeO₅; $a = 15.69$, $b = 5.492$, $c = 3.383$, Å.
Bi₂SiO₅; $a = 15.19$, $b = 5.498$, $c = 3.314$, Å.
Cell content: 4 formula units Bi₂GeO₅ (Bi₂SiO₅).

Final coordinates, isotropic temperature factors and standard deviations resulting from the least-squares refinement of the structure of Bi₂GeO₅, $R = 14.0 \%$, absent reflections included.
Both structures may formally be regarded as being built up of endless chains GeO₅⁻⁻ or SiO₅⁻⁻ and of sheets of the composition Bi₂O₅⁺⁺.

The distances Ge-O within the tetrahedra range from 1.67 ± 0.11 Å to 1.84 ± 0.10 Å and the corresponding angles from 107° ± 5° to 112° ± 5°. The shortest distance O-O within the GeO₅⁻⁻ chain is 2.83 ± 0.10 Å. The chains run along the $c$ axis of the unit cell and the lengths of their repeat units are equal to $c$. The infinite chain in Bi₂GeO₅ is shown in Fig. 1. The ion RO₅⁻⁻ is very similar to the ion SiO₅⁻⁻, found in the silicate diopside (CaMg(SiO₅)₂).³

The bismuth atoms and the oxygen atoms (O₂) in the layer of oxygen atoms at $x = 0.25$ form deformed Bi₂O₅⁺⁺ layers (Fig. 1). The shortest distance bismuth-bismuth within them is 3.600 ± 0.003 Å. The bismuth atoms are in close contact only with three out of four possible oxygen atoms, however. The distances bismuth-oxygen (O₃) within the layers are 2.15,
2.25, 2.28, and 2.66 Å with standard deviations of 0.05 Å, and the shortest oxygen-oxygen distance is 2.66 ± 0.09 Å. The coordination of the bismuth atoms in the deformed layers shows thus a significant difference from what is expected for an ideal Bi₂O₅⁺² layer. The description of the structure as being built up of separate chains GeO₂⁻ and separate layers Bi₂O₅⁺² is therefore too simplified.

A full account of the present work will appear in a forthcoming paper.

These studies form part of a research program on bismuth oxide salts financially supported by the Swedish Natural Research Council.


Received July 24, 1964

Are Aqueous Metavanadate Species Trinuclear, Tetranuclear, or Both? Preliminary LETAGROP Recalculation of Emf Data

FELIPE BRITO, NILS INGRI and LARS GUNNAR SILLEN

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

A few years ago the present authors published 1,2 some emf measurements on metavanadate solutions at 25°C, in alkaline 0.5 M Na(Cl) medium. In these measurements, the average charge, z, per vanadium was varied between −1 (“metavanadate”) and −2 (“pyrovanadate”) and the total vanadium concentration, B, ranged from 0.00062 to 0.0800 M.

An analysis of these data, mainly using graphical methods, indicated that the principal species are, in our notation, B²⁻ (e.g. VO₄(OH)₂⁻ or HVO₄²⁻), H₂B⁺³ (e.g. H₂VO₄⁺), H₃B⁺⁴ (e.g. VO₂⁺), in other words the (0,1), (1,2) and (3,3) species. There was also evidence for the mononuclear (1,1) complex HB⁻ (e.g. VO₃⁻).

We have written for brevity each vanadate complex in the general formula H₃B⁺ₙ(OH)ₙ⁻⁻, and denoted it by the set $(p,q)$. The formation constants $β_{pq}$ (pH₂O + qB⁻ → $H_pB_q(OH)_{2p}^{-q}$ + pOH⁻) and the final set proposed in these studies are shown in the first line of Table 1.

For the main “metavanadate” species (with z = −1), one group of workers have proposed $H_2B_2O_7^-$ (Refs.1,7) and another $H_3B_3O_7^-$ (Refs.8,9,11-13). The strongest indications for the (4,4) species come from freezing-point measurement such as those of Jahn and coworkers 12 (B between 0.20 and 0.35 M) (Ref.12) or between 0.14 and 0.35 M (Ref.13) and Nauman and Hallada 16 (B between 0.027 and 0.195 M).

The emf data of Schwarzenbach and Geiger 14 and spectrophotometric data of Schiller and Thio 15 have been interpreted by trimuclear species. On the other hand, Lefebvre 10 and Šannikov and coworkers 17 have interpreted their emf measurements assuming the species (0,1), (0,2) and (4,4), Lefebvre in addition also (1,2) and (2,4).

In order to test whether our emf data could be explained equally well, assuming the (4,4) species instead of (3,3), we recently 18 carried out an analysis by means of LETAGROP. 19 In LETAGROP, the computer searches — for any combination of complexes — the combination of equilibrium constants $β_{pq}$ that minimizes the error square sum

$$U = Σ(Z_{exp} - Z_{calc})^2 = σ^2(Z).$$

(degrees of freedom).

The closeness of the fit can thus be measured by $U$ or $σ$. In a recent version of LETAGROP, including operations VRID and MIKO, a complex is automatically sorted out (equilibrium constants set = 0) if the minimum would be found for a negative value for this constant.

Using an early version of the LETAGROP program, we have tried 19 various combinations. As seen from Table 1, the combination (1,1) + (1,2) + (3,3) gives a much lower value for $σ(Z)$ than (1,1) + (1,2) + (4,4); (1,1) + (4,4) + (0,2); (1,1) + (4,4); or (1,1) + (3,3).

We have continued these calculations on our 25°C data using the version with MIKO, and some preliminary results are given in Table 1. The computer first rejected (4,4) when it was added to the earlier complexes (1,1) + (1,2) + (3,3) since a positive $β_{44}$ gave no improvement in U. On the other hand, some improvement was found by adding (0,2), and when then the combination with (4,4),

Acta Chem. Scand. 18 (1964) No. 6