Table 1.

Atom	$x \pm \sigma_x$	$y \pm \sigma_y$	$z \pm \sigma_z$	$B \pm \sigma_B$ Å²
Bi_1	0.88945 ± 0.00016	0.10690 ± 0.00018	0.24595 ± 0.00019	1.711 ± 0.019
N_1	0.38748 ± 0.00458	0.11343 ± 0.00501	0.26855 ± 0.00571	2.277 ± 0.584
F_1	0.08350 ± 0.00306	0.14232 ± 0.00336	0.54453 ± 0.00388	2.100 ± 0.365
F_2	0.72081 ± 0.00309	0.17982 ± 0.00349	0.49744 ± 0.00376	2.297 ± 0.380
F_3	0.90583 ± 0.00245	0.07342 ± 0.00268	0.87537 ± 0.00306	1.229 ± 0.264
F_4	0.32291 ± 0.00365	0.04674 ± 0.00404	0.85739 ± 0.00444	2.864 ± 0.448
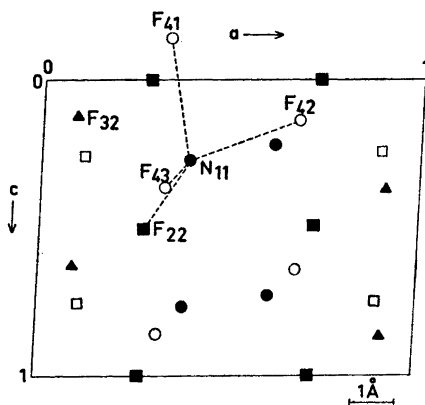
Fig. 2. Projection of the structure of NH_4BiF_4 on the *ac* plane. Notations: Bi □; N ●; F_2 ■; F_3 ▲; F_4 ○. Possible directions of the bonds F--H-N are shown by dashed lines. The atoms are numbered as in Fig. 1.

hydrogen atoms from neutron powder data have not yet been successful.

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

These studies form part of a research program on bismuth compounds containing fluorine, financially supported by the *Swedish Natural Science Research Council*.

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The Crystal Structure of Bi_2GeO_5

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The investigation of the crystal structures of Bi_2GeO_5 and Bi_2SiO_5 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 Bi_2O_3-GeO_2 and Bi_2O_3-SiO_2[1,2] have not reported these phases.

Single crystals of Bi_2GeO_5 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: $Cmc2_1$ (No. 36).
8 Bi, 8 O_2 and 8 O_3 in 8(b):
$(0,0,0;\frac{1}{2},\frac{1}{2},0) + x,y,z; \bar{x},y,z; \bar{x},\bar{y},\frac{1}{2}+z;$
$x,\bar{y},\frac{1}{2}+z.$
4 Ge (Si) and 4 O_1 in 4(a):
$(0,0,0;\frac{1}{2},\frac{1}{2},0) + 0,y,z; 0,\bar{y},\frac{1}{2}+z.$

Table 1.

Atom	$x \pm \sigma_x$	$y \pm \sigma_y$	$z \pm \sigma_z$	$B \pm \sigma_B$ Å²
Bi	0.16758 ± 0.00013	0.21738 ± 0.00043	0.25000	1.192 ± 0.042
Ge	0	0.68572 ± 0.00209	0.20003 ± 0.00219	1.083 ± 0.188
O_1	0	0.5803 ± 0.0161	0.4908 ± 0.0197	1.98 ± 1.47
O_2	0.0949 ± 0.0026	0.1368 ± 0.0085	0.6482 ± 0.0108	0.35 ± 0.64
O_3	0.2541 ± 0.0021	0.4777 ± 0.0079	0.4621 ± 0.0104	0.44 ± 0.70

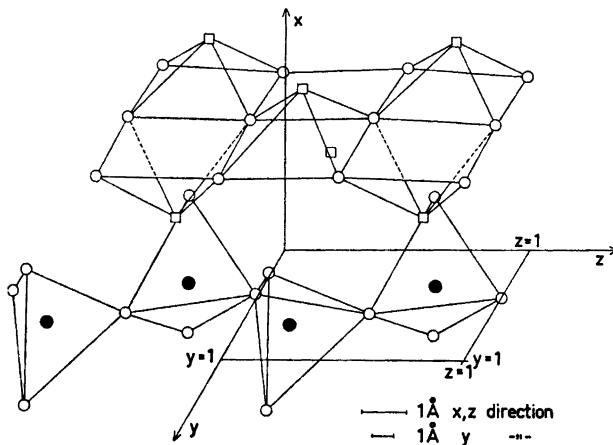*Fig. 1.* Perspective view of the content of one unit cell of Bi_2GeO_5 from $x = 0$ to $x = 0.33$, showing the deformed $Bi_2O_2^{2+}$ layers and the GeO_3^{2-} chains.

Notations: Bi □; Ge ●; O O.

The Bi atoms are connected by full lines with their closest oxygen atom neighbours in the $Bi_2O_2^{2+}$ layer. The linked GeO_4 tetrahedra are also shown by full lines. The axes correspond to the crystallographic ones.

Unit-cell dimensions: Bi_2GeO_5; $a = 15.69_7$ Å, $b = 5.492_8$ Å, $c = 5.383_6$ Å. Bi_2SiO_5; $a = 15.19_5$ Å, $b = 5.468_0$ Å, $c = 5.314_8$ Å.

Cell content: 4 formula units Bi_2GeO_5 (Bi_2SiO_5).

Final coordinates, isotropic temperature factors and standard deviations resulting from the least-squares refinement of the structure of Bi_2GeO_5. $R = 14.0$ %, absent reflections included.

Both structures may formally be regarded as being built up of endless chains GeO_3^{2-} or SiO_3^{2-} and of sheets of the composition $Bi_2O_2^{2+}$.

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 $107° \pm 5°$ to $112° \pm 5°$. The shortest distance O-O within the GeO_3^{2-} 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 Bi_2GeO_5 is shown in Fig. 1. The ion RO_3^{2-} is very similar to the ion SiO_3^{2-}, found in the silicate *diopside* ($CaMg(SiO_3)_2$).[3]

The bismuth atoms and the oxygen atoms (O_3) in the layer of oxygen atoms at $x = 0.25$ form deformed $Bi_2O_2^{2+}$ 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 (O_3) 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 $Bi_2O_2^{2+}$ layer. The description of the structure as being built up of *separate* chains GeO_3^{2-} and *separate* layers $Bi_2O_2^{2+}$ 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*.

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

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A few years ago the present authors published [1,2] some emf measurements on vanadate 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_5 to 0.0800 M.

An analysis of these data, mainly using graphical methods, indicated that the principal species are, in our notation, B^{2-} (*e.g.* $VO_2(OH)_3^{2-}$ or HVO_4^{2-}), HB_2^{3-} (*e.g.* $HV_2O_7^{3-}$) and $H_3B_3^{3-}$ (*e.g.* $V_3O_9^{3-}$), 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.* VO_3^-).

We have written for brevity each vanadate complex in the general formula $H_pB_q^{(2q-p)-}$, and denoted it by the set (p,q). The formation constants β_{pq} $(pH_2O + qB^{2-} \rightleftharpoons H_pB_q^{(2q-p)-} + pOH^-)$ 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 $H_3B_3^{3-}$ (Refs.[3-7]) and another $H_4B_4^{4-}$ (Refs.[8,9,11-13]). The strongest indications for the (4,4) species come from freezing-point measurement such as those of Jahr and coworkers [12] (B between 0.20 and 0.35 M) (Ref.[12a]) or between 0.14 and 0.35 M (Ref.[12b]) 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 Thilo [15] have been interpreted by trinuclear species. On the other hand, Lefebvre [10] and Sannikov 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 wether our emf data could be explained equally well, assuming the (4,4) species instead of (3,3), we recently [20] carried out an analysis by means of LETAGROP.[18] In LETAGROP, the computer searches — for any combination of complexes — the combination of equilibrium constants β_{pq} that minimizes the error square sum

$$U = \Sigma(Z_{exp} - Z_{calc})^2 = \sigma^2(Z). \text{ (degrees of freedom)}.$$

The closeness of the fit can thus be measured by U or σ. In a recent version of LETAGROP,[19] 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,[18] we have tried [20] various combinations. As seen from Table 1, the combination $(1,1) + (1,2) + (3,3)$ gives a much lower value for $\sigma(Z)$ 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),