

Short Communications

On the Crystal Structure of
Dodecahydroxohexabismuth(III)
Perchlorate

BENGT SUNDVALL

Department of Inorganic Chemistry,
Royal Institute of Technology,
S-100 44 Stockholm 70, Sweden

Bismuth(III) is strongly hydrolyzed, even in highly acidic solutions, and several different suggestions¹ have been made as to which hydrolysis products are formed. In 1957 Olin,² from accurate emf measurements on bismuth perchlorate solutions, concluded that $\text{Bi}_6(\text{OH})_{12}^{6+}$ is the predominant species over a wide range of bismuth and hydrogen ion concentrations. At the same time, ultracentrifuge measurements on hydrolyzed bismuth perchlorate solutions by Holmberg, Kraus, and Johnson³ were interpreted as indicating the occurrence of a monodisperse polymer $(\text{BiO})_N^{N+}$, with $N=5$ or 6. Later measurements by Tobias and Tyree⁴ (light scattering), by Levy, Danford, and Agron⁵ (solution X-ray scattering), and by Maroni and Spiro⁶ (Raman spectra on solutions and Raman and infrared spectra on crystals) are all consistent with Olin's results. From their solution X-ray measurements, Levy *et al.* concluded that the arrangement of Bi atoms in the complex is octahedral with short Bi—Bi distances of 3.70 Å. Maroni and Spiro⁷ showed that such a model is also consistent with Raman and IR spectra.

Gattow and Kiel,⁸ in a crystal structure study on the basic nitrate $\text{BiONO}_3(\text{H}_2\text{O})_{1/2}$, found isolated hexanuclear complexes forming trigonal prisms (only bismuth positions were determined). In other crystal structure investigations of basic bismuth salts, for example work by Aurivillius and co-workers,^{9,10} the bismuth atoms have been found to form infinite layers together with oxygen.

It has been found in the work described here that discrete complexes, with an octahedral arrangement of Bi atoms, exist in crystals grown from hydrolyzed bismuth perchlorate solutions. The crystals can be prepared by dissolving Bi_2O_3 in 3 M HClO_4 in a molar ratio $\text{Bi}_2\text{O}_3:\text{HClO}_4=1:2$, and crystallizing under a heating lamp. The colourless, well-shaped rhombic crystals are very deliquescent. For X-ray

measurements they were transferred directly from the mother-liquor into capillaries, which were then sealed. Even then they were found to decompose during long exposure to an X-ray beam.

Analyses for Bi and ClO_4^- showed the composition of the crystals to correspond to $\text{Bi}_2\text{O}_3:\text{Cl}_2\text{O}_7:x\text{H}_2\text{O}$ with $x\approx 2$. The results of a crystal structure analysis show that the formula should probably be written $\text{Bi}(\text{OH})_2\text{ClO}_4$.

Oscillation and Weissenberg X-ray diffraction photographs taken with $\text{CuK}\alpha$ -radiation from a 0.1 mm long crystal oscillated about two different axes, show the crystal system to be orthorhombic. The unit cell constants derived from these photographs and Guinier powder photographs are $a=11.103(2)$ Å, $b=16.983(4)$ Å, $c=17.405(4)$ Å.

The calculated density assuming 24 formula weights in the unit cell is 4.16 g cm^{-3} . The observed density as determined by a weight-loss method is 4.24 g cm^{-3} . Systematically absent reflexions uniquely indicate the space-group to be $P2_12_12_1$. The positions of the Bi atoms were derived from a three-dimensional Patterson synthesis calculated using 1420 visually estimated intensities. No corrections were made for absorption. Least squares refinement of the Bi parameters led to an R-factor of 0.20 and the positional and thermal parameter values given in Table 1. Fourier maps confirm the correctness of the derived Bi positions.

Projections of the positions of the Bi atoms on the bc - and the ab -planes are shown in Fig. 1. The six bismuth atoms in the asymmetric unit form a slightly distorted octahedron, and four such octahedra are present in the unit cell. The Bi—Bi distances within each octahedron

Table 1. Fractional coordinates with e.s.d.'s in paranthesis and isotropic temperature factors.

| | x | y | z | $B(\text{Å}^2)$ |
|-------|-----------|-----------|-----------|-----------------|
| Bi(1) | 0.0614(6) | 0.1677(6) | 0.3478(4) | 1.7 |
| Bi(2) | 0.1293(6) | 0.0886(6) | 0.1525(3) | 1.5 |
| Bi(3) | 0.4476(6) | 0.1487(6) | 0.1781(3) | 1.5 |
| Bi(4) | 0.2055(6) | 0.2914(6) | 0.2034(3) | 1.7 |
| Bi(5) | 0.3020(7) | 0.0167(6) | 0.3161(4) | 1.9 |
| Bi(6) | 0.3795(6) | 0.2161(6) | 0.3750(3) | 1.5 |

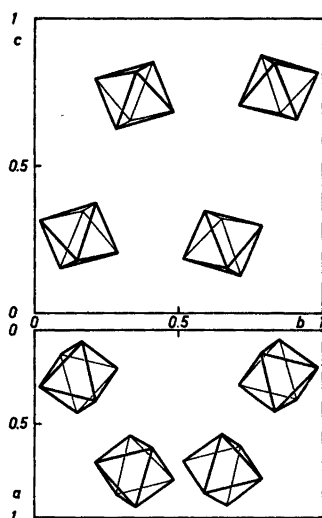


Fig. 1. Projection of the positions of Bi-atoms in one unit cell of $\text{Bi}_6(\text{OH})_{12}(\text{ClO}_4)_6$ on the bc -plane (upper part) and on the ab -plane (lower part).

range from 3.64(1) to 3.77(1) Å along the edges, and from 5.18(1) to 5.22(1) Å along the diagonals. The shortest Bi–Bi distance between two different octahedra is 8.78(2) Å, clearly showing that the crystal contains discrete hexanuclear bismuth complexes. The Bi–Bi distances found are close to the corresponding distance of 3.70 Å deduced by Levy *et al.* for the complexes in solution.

A complete structure determination is in progress.

Acknowledgement. The work has been financially supported by the Swedish Natural Science Research Council. The English text has been revised by Dr. Derek Lewis.

- Sillén, L. G. and Martell, A. *Stability Constants of Metal-Ion Complexes*, Special Publication No. 17, The Chemical Society, London 1964.
- Olin, Å. *Acta Chem. Scand.* 11 (1957) 1445.
- Holmberg, R. W., Kraus, K. A. and Johnson, J. S. *J. Amer. Chem. Soc.* 78 (1956) 5506.
- Tobias, R. S. and Tyree, S. Y. *J. Amer. Chem. Soc.* 82 (1960) 3244.
- Levy, H. A., Danford, M. D. and Agron, P. A. *J. Chem. Phys.* 31 (1959) 1458.
- Maroni, V. A. and Spiro, T. G. *J. Amer. Chem. Soc.* 88 (1966) 1410.
- Maroni, V. A. and Spiro, T. G. *Inorg. Chem.* 7 (1968) 183.

- Gattow, G. and Kiel, G. *Naturwissenschaften* 55 (1968) 389.
- Aurivillius, B. and Löwenhielm, A. *Acta Chem. Scand.* 18 (1964) 1937.
- Aurivillius, B. *Acta Chem. Scand.* 18 (1964) 2375.

Received May 21, 1974.

Structure of Gaseous Dimethyltrithiocarbonate Studied by Electron Diffraction

A. ALMENNINGEN,^a L. FERNHOLT,^a
H. M. SEIP^a and L. HENRIKSEN^b

^a Department of Chemistry, University of Oslo, Oslo 3, Norway, ^b Department of General and Organic Chemistry, The H. C. Ørsted Institute, University of Copenhagen, Copenhagen Ø, Denmark

Methyl vinyl sulfide has been shown by electron-diffraction^{1,2} and by vibrational spectroscopy^{3,4} to exist in two conformers, one *syn* (or *cis*) form and a *gauche* form with a non-planar skeleton. The infrared and Raman spectra of liquid and cryst. dimethyltrithiocarbonate, $\text{S}=\text{C}(\text{SCH}_3)_2$, have been reported^{5,6} and the presence of two conformers was found in the liquid state. As a part of a study of the conformational properties of molecules with $\text{C}(sp^2)\text{--S}$ bonds, we have investigated dimethyltrithiocarbonate by means of electron-diffraction measurements.

The electron-diffraction data were recorded with the Oslo apparatus.⁷ A modified molecular intensity curve ranging from $s=1.50 \text{ \AA}^{-1}$ to $s=41.0 \text{ \AA}^{-1}$, was obtained in the usual way.⁸ The experimental radial distribution (RD) function obtained by Fourier inversion of the intensity curve, is shown in Fig. 1.

The most likely conformers for this molecule are the *syn-syn* form shown in Fig. 1, a *syn-anti* form which also has a planar skeleton, and non-planar forms, e.g. *syn-gauche* or *gauche-gauche*. Calculations of theoretical RD functions showed that only the *syn-syn* form was consistent with the electron-diffraction data. Least-squares refinements were therefore carried out assuming this model.

The simple force field given in Table 1, which yielded frequencies in reasonable agree-