mimics for copper enzymes or copper nonenzymatic proteins, especially for "blue proteins" of type 2 Cu.[22]

Acknowledgment. The authors are grateful to the Centro Strumenti dell'Universitâ di Modena for the recording of the infrared spectra.

Registry No. $Cu(TsglyH)_2(Im)_2$, 85479-91-0; $Cu(TsglyH)_2$(*N*-$MeIm)_2$, 85479-92-1; $Cu(TsglyH)_2(py)_2$, 85506-84-9; $Cu(TsglyH)_2 \cdot 4H_2O$, 85337-91-3.

Supplementary Material Available: Listings of selected least-squares planes, distances involving hydrogen atoms, bond distances and angles in tosylate benzene rings, and final structure factors (17 pages). Ordering information is given on any current masthead page.

---

[22] Beinert, H. *Coord. Chem. Rev.* **1980**, *33*, 55.

Contribution from the Department of Inorganic Chemistry,
The Royal Institute of Technology, Stockholm, Sweden

Crystal Structure of Tetraoxotetrahydroxohexabismuth(III) Perchlorate Heptahydrate, $Bi_6O_4(HO)_4(ClO_4)_6 \cdot 7H_2O$: An X-ray and Neutron Diffraction Study

BENGT SUNDVALL

Received July 17, 1982

The structure of the title compound was determined from single-crystal X-ray and neutron diffraction data, collected by diffractometric methods. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with $Z = 4$, $a = 11.084$ (3) Å, $b = 16.992$ (2) Å, and $c = 17.387$ (3) Å. The structure was derived on the basis of the intensities of 3183 X-ray and 2679 neutron reflections by using Patterson and Fourier methods. Refinement by full-matrix least-squares methods gave the conventional R values 0.067 (X-rays) and 0.087 (neutrons). The structure contains discrete hexanuclear complexes $Bi_6O_4(HO)_4{}^{6+}$, $ClO_4{}^-$ ions, and crystal water molecules. The bismuth complex has a slightly distorted octahedral arrangement of the Bi atoms, with the O atoms located above the octahedral faces. Each type of oxygen (oxide and hydroxide) forms a distorted tetrahedron surrounding the Bi octahedron, giving close to T_d symmetry of the complex. The short Bi---Bi distances in the complex vary between 3.633 (8) and 3.764 (8) Å (average 3.675 Å), the short Bi---O^{2-} distances between 2.10 (1) and 2.20 (1) Å (average 2.15 Å), and the short Bi---OH^- distances between 2.29 (1) and 2.48 (1) Å (average 2.40 Å). The coordination of oxygen to Bi within the complex is trigonal bipyramidal, with the hydroxide oxygens at the axial apices and the oxide oxygens at two of the equatorial apices, the third being occupied by the lone $6s^2$ electron pair of Bi. Each Bi coordinates four other oxygen atoms outside the complex at longer Bi---O distances, giving a total coordination number of 8. The coordination polyhedra are irregular. Infrared and Raman spectra of the complex both in solid state and in solution are consistent with this structure. All but three of the hydrogen atoms participate in hydrogen bonds, most of which are weak. The perchlorate ions are close to tetrahedral with an average Cl---O distance of 1.44 Å, the individual distances having estimated standard deviations of 0.01 Å.

Introduction

Several independent methods have proved that the main species in moderately acidic solutions of bismuth(III) over a wide range of metal concentrations is a hexanuclear complex. Reviews of the work are given in ref 1 and 2.

From the results of emf measurements, the formula $Bi_6(HO)_{12}{}^{6+}$ was proposed,[3] with the reservation that the emf method cannot distinguish between this formula and others with different numbers of water molecules. The occurrence of a hexanuclear species was confirmed in an X-ray solution study,[4] where the metal atoms were found to have an octahedral arrangement and the bridging HO^- groups were assumed to be located above the octahedral edges. The oxygen atoms could not, however, be located with precision. Raman measurements on solutions and crystals of the perchlorate, as well as infrared measurements on crystals,[5,6] were interpreted by the same formula and geometric arrangement.

In an X-ray structure study[7] of the basic bismuth nitrate $BiONO_3 \cdot {}^1/_2H_2O$, an alternative structure was suggested. The structure was proposed to contain hexanuclear aggregates of bismuth atoms, forming trigonal prisms. The light atoms could not be located, and no refinement of the Bi positions was performed. A reinvestigation[8] of the structure of this salt showed the proposed structure to be in error. It contains complexes $Bi_6O_4(HO)_4{}^{6+}$, very similar to those found in the present work, and the formula should accordingly be written $Bi_6O_4(HO)_4(NO_3)_6 \cdot H_2O$.

This was confirmed by a simultaneous, independent investigation[9] by Lazarini. Virtually the only difference is that Lazarini, in view of IR spectroscopy[10] and TGA results,[11] considered also the water molecule and a nitrate group to be coordinated to Bi, i.e. writing the formula of the complex $[Bi_6(H_2O)(NO_3)O_4(HO)_4]^{5+}$.

Lazarini also found the same arrangement of Bi and O in two other structures. The compound $Bi_6O_4(HO)_4(NO_3)_6 \cdot 4H_2O$[12] contains isolated $Bi_6O_4(HO)_4{}^{6+}$ units while in $Bi_6O_5(HO)_3(NO_3)_5 \cdot 3H_2O$[13] there is a closely related complex $Bi_6O_5(HO)_3{}^{5+}$. In the latter compound the hexanuclear groups are linked in pairs through two intermolecular Bi---O bonds.

The present study has been undertaken in order to obtain more extensive structural evidence for the composition and geometry of the hexanuclear bismuth hydrolysis complex. A preliminary X-ray investigation of the basic perchlorate salt using film methods has been published earlier,[14] in which it was shown that the Bi atoms form discrete hexanuclear complexes with octahedral geometry.

---

(1) F. Granér and L. G. Sillén, *Acta Chem. Scand.*, **1**, 631 (1947).
(2) C. F. Baes, Jr., and R. E. Mesmer, "The Hydrolysis of Cations", Wiley, New York, 1976.
(3) Å. Olin, *Acta Chem. Scand.*, **11**, 1445 (1957).
(4) H. A. Levy, M. D. Danford, and P. A. Agron, *J. Chem. Phys.*, **31**, 1458 (1959).
(5) V. A. Maroni and T. G. Spiro, *J. Am. Chem. Soc.*, **88**, 1410 (1966).
(6) V. A. Maroni and T. G. Spiro, *Inorg. Chem.*, **7**, 183 (1968).
(7) G. Kiel and G. Gattow, *Naturwissenschaften*, **55**, 389 (1968).
(8) B. Sundvall, *Acta Chem. Scand., Ser. A*, **A33**, 219 (1979).
(9) F. Lazarini, *Acta Crystallogr., Sect. B*, **B35**, 448 (1979).
(10) G. Kiel, Thesis, Georg-August-Universität, Göttingen, 1967.
(11) F. Lazarini, personal communication.
(12) F. Lazarini, *Cryst. Struct. Commun.*, **8**, 69 (1979).
(13) F. Lazarini, *Acta Crystallogr., Sect. B*, **B34**, 3169 (1978).
(14) B. Sundvall, *Acta Chem. Scand., Ser. A*, **A28**, 1036 (1974).
(15) R. Tellgren, *Acta Univ. Ups. Abstr. Uppsala Diss. Fac. Sci.*, **No. 344** (1975).

0020-1669/83/1322-1906$01.50/0 © 1983 American Chemical Society

Experimental Section

Preparation and Analysis. A solution with the mole ratio Bi:ClO_4 = 1:1 was prepared by dissolving purified Bi_2O_3 in 3 M $HClO_4$. Well-shaped single crystals of a size suitable for the X-ray measurements could be obtained by crystallization of a few drops of the viscous saturated solution on a glass plate in air of low humidity. The crystals are deliquescent and had to be kept in sealed, thin-walled capillary tubes.

Large single crystals for the neutron diffraction measurements were obtained by slow evaporation of a solution from a beaker covered with thin polythene film. Unfortunately, the crystals grew concave on the crystal side facing the bottom of the beaker and had to be ground planar. The crystal chosen for study was protected from humidity by means of a thin-walled quartz bulb, which has a negligible neutron absorption.

The analysis of the solid was complicated by the fact that the crystals apparently lost crystal water when dried in a desiccator. A determination of the mole ratio Bi:ClO_4 could be accomplished by dissolving a known amount of cautiously dried crystals in water and determining Bi as phosphate and the perchlorate by ion exchange. The mole ratio was 1:1 within 0.4%, corresponding to the stoichiometric formula $BiOClO_4{\cdot}xH_2O$. The water content was estimated by growing relatively large crystals, which were dried in a desiccator until the crystal faces just grew opaque. After being weighed, the crystals were heated at 120 °C to constant weight. The weight loss corresponded to seven water molecules per hexanuclear unit, a result which was later confirmed by the structure determination. The density was determined by the apparent loss of weight in benzene of large crystals, dried as described above. The experimental value, 4.24 g cm^{-3}, agrees well with the calculated value, 4.277 (2) g cm^{-3}.

Intensity Data Collection. Details of the data collection and reduction and the refinement procedures are summarized in Table I for both the X-ray and the neutron diffraction measurements.

The space group and the positions of the Bi atoms were obtained from the study of the structure by using the Weissenberg film technique.[14] These data were not, however, accurate enough to reveal the light atoms.

A new set of X-ray intensity data were collected at 25 °C on a Syntex $P2_1$ four-circle diffractometer controlled by a NOVA computer. The orientation of the arbitrarily mounted crystal was determined as described previously.[16] Accurate cell parameters were determined by using 25 reflections with $2\theta > 40°$.

The neutron diffraction intensity data were recorded by a Hilger and Watts four-circle diffractometer, controlled by a PDP8 computer. The neutron source was the Swedish Atomic Energy reactor R2 at Studsvik. After about 1800 recorded reflections, the intensities of the check reflections began to exhibit a slow, continuous decrease. During a summer break at the reactor, the intensities dropped 30% and continued to decrease during the remaining part of the data collection. The reason for this was later found to be a deterioration of the lower part of the crystal, caused by the glue used to attach the crystal to the specimen holder. An attempt to correct for the intensity decay was made by least-squares fittings of the intensities of the check reflections as a function of exposure time. To each measured reflection a mean correction factor, based on this correction, was applied.

Structure Solution and Refinement

All refinements, both in the X-ray and in the neutron diffraction experiments, were performed by using the full-matrix least-squares method.

X-ray Data. From a difference Fourier synthesis, using all reflections (including zero-weight data) and phased on the isotropically refined Bi parameters obtained in the film measurements, the positions of eight oxygen atoms in the vicinity of the bismuth octahedron and all the atoms in the perchlorate groups except one oxygen atom could be located. After refinement, a second difference synthesis revealed the missing perchlorate oxygen and seven water oxygens.

Table I. Conditions for Data Collection, Data Reduction, and Refinement

Intensity Data Collection

crystal habit: X-rays, rhombic tabular (001), boundary faces (001), $(00\bar{1})$, (110), $(1\bar{1}0)$, $(\bar{1}10)$, $(\bar{1}\bar{1}0)$, volume 0.001 16 mm^3; neutrons, rhombic tabular (001), boundary faces (001), $(00\bar{1})$, (110), $(\bar{1}10)$, $(1\bar{1}0)$, $(\bar{1}\bar{1}0)$, (010), $(0\bar{1}0)$, (011), volume 53.6 mm^3
radiation: X-rays, graphite-monochromatized Mo Kα, λ = 0.710 69 Å; neutrons, copper monochromatized,[15] λ = 1.210 (5) Å, flux 9×10^5 neutrons cm^{-2} s^{-1}
part of the reflection sphere investigated: X-rays, octant, $2\theta \leqslant 53°$; neutrons, quadrant, $2\theta \leqslant 40°$, octant $40° \leqslant 2\theta \leqslant 90°$
scan technique: X-rays, ω-scan, scan range 1°, variable intensity-dependent scan speed; neutrons, ω-scan, scan range 2.5°, steps 0.05°

Background Correction, Intensity, and Standard Deviation

computation: X-rays, ref 16; neutrons,[a] peak-profile analysis[17]
check reflections: X-rays, four after each 40th reflection, constant intensity within 6%; neutrons, three after each 50th reflection, intensity decay, see text

Data Reduction

absorption correction: X-rays, comparison of (1) semiempirical method,[16,19] computer program XTL,[20] and (2) Gaussian integration method,[21] computer program DATAPU,[18] with a relative transmission factor variation in both cases within the ratio 1:0.2;[b] neutrons, Gaussian integration method,[21] computer program DATAPU,[18] with a transmission factor variation 0.57-0.78, experimentally determined μ = 1.351 cm^{-1}
Lorentz and polarization corrections: X-rays and neutrons
extinction correction: X-rays, no correction; neutrons, correction applied in the refinement process by using an isotropic extinction coefficient g in the expression $|F_o|_{cor} = |F_o|[1 + 2\bar{T}|F_c|^2 g\lambda^3 V^{-2}(\sin 2\theta)^{-1}]^{1/4}$ ($\bar{T}$ = mean path length), refined value g = 2060 (570), extinction factor variation 1.00-1.07

Full-Matrix, Least-Squares Refinement

computer programs: X-rays, XTL;[20] neutrons, UPALS[18]
scattering factors: X-rays, scattering factors for neutral atoms,[22] Bi and Cl corrected for anomalous dispersion;[22] neutrons, scattering amplitudes in ref 22
no. of reflections, m: X-rays, unique data set, $m = 3183$ (4384^c); neutrons, no averaging of equivalent reflections, all data used in the structure determination, $m = 2679$ (3424^c), no. of independent reflections = 3070
no. of parameters refined, n: X-rays, $n = 325$; neutrons, $n = 416$
function minimized: X-rays and neutrons, $\Sigma w_i(|F_o| - k|F_c|)^2$
weights[d] ($w_i = [\sigma_{c,i}^2(F_o) + (CF_o)^2]^{-1}$, $\sigma_{c,i}$ = statistically based standard deviation); X-rays, $C = 0.03$; neutrons, $C = 0.02$
limit defining unobserved reflections: X-rays and neutrons, reflections with $|F_o| \leqslant 3.92\sigma_c(F_o)$ were given zero weight

Agreement Factors

$R = \Sigma|F_o - kF_c|/\Sigma|F_o|$: X-rays,[e] $R = 0.067$ (0.098^c); neutrons, $R = 0.087$ (0.128^c)
$R_w = [\Sigma w_i|F_o - kF_c|^2/\Sigma w_i F_o^2]^{1/2}$: X-rays,[e] $R_w = 0.068$ (0.074^c); neutrons, $R_w = 0.119$ (0.209^c)
$S = [\Sigma w_i|F_o - kF_c|^2/(m - n)]^{1/2}$: X-rays, $S = 1.312$; neutrons, $S = 2.646$

[a] Most of the reflections showed double peaks, probably due to a crack in the crystal. The intensities of both peaks were used in the structure determination. For some hundreds of reflections, the program could not handle the background correction due to overlap between peak and background. These were calculated by hand. [b] In general, the resulting F_o values from the two corrected data sets agreed within $3\sigma_c(F_o)$; for a few strong reflections, the Gaussian integration method gave higher values of F_o; greatest difference was $6\sigma_c(F_o)$. [c] Including zero-weight data. [d] The weighting functions were chosen to given an acceptable weighting scheme, i.e. an even distribution of the error function S or the quantity $w_i|F_o - F_c|^2$ with respect to F_o and $(\sin\theta)/\lambda$. [e] Absorption correction by the semiempirical method.

---

(16) M. Sandström and I. Persson, *Acta Chem. Scand., Ser. A*, **A32**, 95 (1978).
(17) M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect. A*, **A30**, 580 (1974).
(18) The computer programs used in the neutron diffraction study, DATAPH, DRF, UPALS, DISTAN, and ORTEP, are described in a summary by J. O. Lundgren, "Crystallographic Program Report UUIC-B13-4-02", Institute of Chemistry, University of Uppsala, Uppsala, Sweden, 1975.
(19) G. Kopfmann and R. Huber, *Acta Crystallogr., Sect. A*, **A24**, 348 (1968).
(20) Standard Syntex XTL Structure Determination System, Syntex Analytical Instruments, Inc., Cupertino, CA 95014.
(21) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).
(22) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.

In the final refinement, the Bi and Cl atoms were given anisotropic thermal parameters while the O atoms were kept isotropic. The parameter shifts in the last cycle were less than 1% of the estimated standard deviations. An attempt to treat all the atoms anisotropically led to negative and thus physically meaningless values of some of the principal temperature factor coefficients.

Two methods of absorption correction were tried (see Table I). They gave about the same result. The semiempirical correction gave a slightly lower R value and in general somewhat lower estimated standard deviations. Refinement without correction for absorption gave a higher residual, $R = 0.119$.

A final difference Fourier synthesis showed spurious peaks near the positions of the heavy atoms. The highest peak was 4.1 e Å^{-3}, which may be compared with 9.1 e Å^{-3} for the lowest oxygen peak in a final electron density map. This residual electron density is probably due mainly to errors in the absorption correction.

Neutron Data. The parameters of the non-hydrogen atoms from the X-ray measurements were used as input into a difference Fourier synthesis. All the expected water hydrogens and four hydrogen atoms bonded to four of the oxygen atoms in the complex could easily be located. No peaks originating from any other unrevealed atom in the X-ray measurements could be found.

The Bi and Cl together with the four H atoms belonging to the complex and twelve of the fourteen water hydrogens could successfully be refined anisotropically. The remaining two water hydrogens received negative temperature coefficients when refined anisotropically and were kept isotropic in the final cycles of refinement. No attempt was made to refine the oxygen atoms anisotropically, since the ratio of the number of observations to the number of refined parameters would then have been too low. Due to the high computational costs, the refinement was stopped when the largest ratio of the parameter shifts to the estimated standard deviations was about 0.25 for the positional parameters and about 0.40 for the temperature coefficients.

A δR plot[23] gave an essentially linear relationship between the observed and the calculated F residuals. The least-squares-fitted line had a slope of 2.13 and an intercept of 0.04 (1.94 and 0.15, respectively, when zero-weight data were included). The high value of the slope implies an underestimation of $\sigma(F_o)$ by at least 100%. This may be compared with the value 2.65 of S, the standard deviation of an observation of unit weight. The data are undoubtedly affected by systematic errors, probably a result of the previously mentioned deterioration of the crystal.

Comparison of X-ray and Neutron Data. The consistency of the structure parameters obtained by the X-ray and the neutron diffraction measurements was tested in a half-normal probability plot,[24] where interatomic distances less than 7.3 Å were compared. The least-squares-fitted line had a slope of 1.11 and an intercept of 0.00, showing a good agreement between the two sets of parameters.

The atomic parameters are given in Tables IIa and IIb (Table IIb is supplementary material). There is no significant difference between either the positional or the thermal parameters of the heavy atoms in the two determinations. Since the light atoms are more accurately determined in the neutron diffraction study, the atomic parameters from this data set were chosen for the calculations of interatomic distances and angles referred to in the following discussion.

Correction for Thermal Motion. Anomalously short O- - -H distances in two of the water molecules indicated that the bond lengths might be affected by the thermal motion of some of the hydrogen atoms. An attempt to correct for this effect was made as described by Busing, Martin, and Levy.[25] The corrections are expected to be largest for the light atoms, but as a check, a calculation was also carried out for the heavy atoms. In the latter case, independent motions of the atoms were assumed. Only minor corrections to the Bi- - -Bi and the Bi- - -O distances were obtained, the order of magnitude being about one estimated standard deviation. Hence, the uncorrected values of these distances are used in the following discussion.

Vibrational Spectra. Raman spectra of a polycrystalline powder and a saturated solution were recorded on a Cary 82 spectrophotometer using the 4880-Å Ar$^+$–Kr$^+$ laser excitation. Slit widths corresponding to 4.0 cm^{-1} were used for the solid and to 5.0 cm^{-1} for the solution. The samples were contained in quartz capillaries.

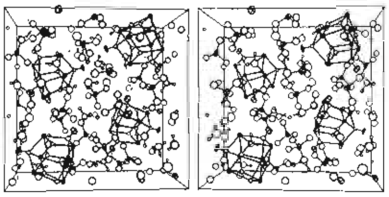

Figure 1. Stereoscopic view of the unit cell contents. Ellipsoids are scaled to include 50% probability, except for the water hydrogens, which for clarity are drawn as isotropic with $B = 0.5$ Å^2. Bi- - -O, Cl- - -O, and H- - -O bonds are drawn as thick single lines, and suggested hydrogen bonds, as thin double lines. The orientation of the cell is as follows: the origin is chosen at the front left corner with the a axis directed into the view, the b axis directed vertically, and the c axis directed horizontally.

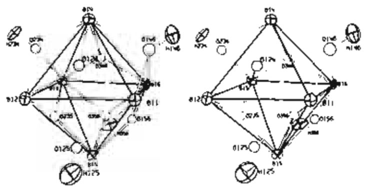

Figure 2. Stereoscopic view of the complex $Bi_6O_4(HO)_4^{6+}$. Ellipsoids are scaled to include 50% probability. The Bi_6 octahedron is marked by thick single lines, not to be interpreted as indicating any Bi- - -Bi bonds.

A low-frequency infrared spectrum was recorded on an RIIC FS-720 Fourier spectrometer. The sample was studied as a mull in Nujol, carried between polyethylene plates at 100 K.

Crystal Data (X-ray Diffraction): $Bi_6O_4(HO)_4(ClO_4)_6 \cdot 7H_2O$; orthorhombic, space group $P2_12_12_1$ (No. 19); $a = 11.0836$ (32), $b = 16.9916$ (47), $c = 17.3871$ (27) Å; $V = 3274.5$ (14) Å^3; $M_r = 2108.72$; $Z = 4$; $D_x = 4.277$ (2), $D_{\text{measd}} = 4.24$ g cm^{-3}; $\mu_x = 311.8$, $\mu_{n,\text{measd}} = 1.351$ cm^{-1}.

Description and Discussion of the Structure

The structure is built from isolated hexanuclear complexes $Bi_6O_4(HO)_4^{6+}$, perchlorate ions, and crystal water molecules. The complexes are kept together by hydrogen bonds and by the perchlorate groups through bismuth–oxygen coordination. These interactions are, however, very weak, and the geometry of the structure is determined mainly by packing effects. The content of one unit cell is shown in Figure 1.

The Complex. The structure of the complex is shown in Figure 2. The interatomic distances and some mean bond distances of interest for the following discussion are listed in Table III.

The six Bi atoms form a slightly distorted octahedron, where the metal atoms are kept together by eight triply coordinated oxygen atoms, each of which is situated above an octahedral face. Four are oxide oxygens, and four are hydroxide oxygens. The Bi–oxide oxygen distances are significantly shorter than the Bi–hydroxide oxygen distances. Each type of oxygen encloses the Bi octahedron in an approximately tetrahedral arrangement, indicating an ideal T_d symmetry of the complex.

This structure is very similar to the M_6X_8 cluster structure of molybdenum and tungsten halides, e.g. $Mo_6Cl_8^{2+}$.[26] The cubic arrangement of the anions is regular in these compounds, but in the present structure it is distorted due to the differences in lengths of the two sets of bismuth–oxygen bonds. A few other structures of metal complexes of this type have been reported: the isostructural compounds $U_6O_4(HO)_4(SO_4)_6$[27] and $Ce_6O_4(HO)_4(SO_4)_6$[28] by Lundgren; the crystalline tin(II)

---

[23] S. C. Abrahams and E. T. Keve, *Acta Crystallogr., Sect. A*, **A27**, 157 (1971).

[24] S. C. Abrahams, *Acta Crystallogr., Sect. A*, **A25**, 165 (1969).

[25] W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.

[26] C. Brosset, *Ark. Kemi, Mineral., Geol.*, **A20** (1945), **A22** (1946).

[27] G. Lundgren, *Ark. Kemi*, **5**, 349 (1953).

[28] G. Lundgren, *Ark. Kemi*, **10**, 183 (1956).

Table IIa. Positional and Isotropic Thermal Parameters and Their Estimated Standard Deviations (in Parentheses) from the X-ray Data (Upper Value) and the Neutron Data (Lower Value)

atom[a]	x	y	z	B, Å²	atom[a]	x	y	z	B, Å²
Bi(1)	0.06209 (15)	0.16509 (10)	0.34807 (8)		O(34)	1.002 (4)	0.380 (2)	0.248 (2)	3.4 (8)
	0.0629 (5)	0.1645 (4)	0.3479 (3)			0.9996 (11)	0.3781 (7)	0.2480 (7)	2.96 (21)
Bi(2)	0.12795 (16)	0.08865 (10)	0.15250 (8)		Cl(4)	0.4919 (11)	0.3432 (8)	0.0646 (6)	
	0.1286 (5)	0.0886 (4)	0.1524 (3)			0.4913 (5)	0.3435 (4)	0.0654 (4)	
Bi(3)	0.44750 (16)	0.14850 (10)	0.17727 (8)		O(41)	0.513 (5)	0.259 (3)	0.072 (2)	4.9 (10)
	0.4475 (5)	0.1487 (4)	0.1773 (3)			0.5156 (12)	0.2576 (8)	0.0729 (8)	3.89 (26)
Bi(4)	0.20515 (15)	0.29134 (10)	0.20320 (8)		O(42)	0.498 (3)	0.362 (2)	−0.012 (2)	2.5 (6)
	0.2053 (5)	0.2902 (3)	0.2035 (3)			0.4959 (12)	0.3582 (8)	−0.0141 (8)	3.88 (25)
Bi(5)	0.30240 (17)	0.01598 (10)	0.31543 (9)		O(43)	0.366 (3)	0.354 (2)	0.093 (2)	2.6 (6)
	0.3033 (5)	0.0151 (4)	0.3140 (3)			0.3719 (10)	0.3571 (7)	0.0941 (7)	2.96 (22)
Bi(6)	0.37994 (16)	0.21531 (10)	0.37445 (8)		O(44)	0.575 (5)	0.383 (3)	0.103 (3)	6.1 (12)
	0.3800 (5)	0.2150 (4)	0.3740 (3)			0.5768 (16)	0.3850 (10)	0.1047 (10)	6.04 (38)
O(124)	0.094 (3)	0.189 (2)	0.225 (2)	1.6 (5)	Cl(5)	0.8730 (12)	0.4680 (8)	0.0127 (6)	
	0.0984 (7)	0.1869 (5)	0.2271 (5)	0.94 (14)		0.8732 (5)	0.4682 (4)	0.0148 (3)	
O(156)	0.242 (3)	0.124 (2)	0.365 (2)	2.2 (6)	O(51)	0.860 (4)	0.432 (2)	0.085 (2)	3.2 (7)
	0.2443 (7)	0.1256 (5)	0.3643 (5)	0.83 (14)		0.8515 (11)	0.4303 (7)	0.0876 (7)	2.95 (22)
O(235)	0.302 (3)	0.066 (2)	0.202 (1)	1.5 (5)	O(52)	0.929 (4)	0.542 (3)	0.025 (2)	4.6 (10)
	0.3005 (7)	0.0665 (5)	0.2041 (5)	1.05 (14)		0.9308 (10)	0.5432 (7)	0.0270 (7)	3.15 (22)
O(346)	0.368 (3)	0.237 (2)	0.248 (1)	0.9 (5)	O(53)	0.950 (4)	0.416 (2)	−0.028 (2)	2.9 (7)
	0.3671 (7)	0.2337 (5)	0.2493 (5)	0.92 (14)		0.9506 (10)	0.4167 (7)	−0.0281 (7)	2.74 (21)
O(125)	0.097 (3)	0.038 (2)	0.278 (1)	0.9 (5)	O(54)	0.763 (4)	0.474 (3)	−0.026 (2)	4.0 (9)
	0.0954 (8)	0.0385 (5)	0.2791 (5)	0.98 (14)		0.7609 (11)	0.4772 (7)	−0.0248 (7)	3.35 (23)
H(125)	0.0399 (16)	−0.0038 (12)	0.2879 (11)		Cl(6)	0.4169 (11)	0.4349 (7)	0.3113 (6)	
O(146)	0.188 (3)	0.274 (2)	0.343 (2)	2.0 (6)		0.4159 (5)	0.4346 (3)	0.3113 (4)	
	0.8120 (8)	0.2747 (6)	0.3424 (6)	1.50 (16)	O(61)	0.429 (4)	0.380 (2)	0.373 (2)	3.3 (8)
H(146)	0.1633 (4)	0.3197 (10)	0.3747 (10)			0.4233 (11)	0.3803 (7)	0.3750 (7)	3.30 (22)
O(243)	0.261 (3)	0.195 (2)	0.115 (1)	1.1 (5)	O(62)	0.417 (3)	0.515 (2)	0.338 (2)	2.9 (7)
	0.2637 (7)	0.1916 (5)	0.1165 (5)	0.94 (14)		0.4141 (11)	0.5126 (8)	0.3388 (7)	3.53 (24)
H(234)	0.2724 (13)	0.2066 (10)	0.0608 (8)		O(63)	0.307 (5)	0.424 (3)	0.269 (2)	5.1 (10)
O(356)	0.467 (3)	0.104 (2)	0.309 (2)	1.8 (6)		0.3064 (10)	0.4175 (7)	0.2711 (7)	2.87 (22)
	0.4678 (9)	0.1053 (6)	0.3078 (5)	1.45 (16)	O(64)	0.515 (4)	0.423 (3)	0.260 (2)	3.3 (8)
H(356)	0.5422 (14)	0.0847 (11)	0.3266 (10)			0.5158 (2)	0.4232 (8)	0.2622 (8)	3.83 (26)
Cl(1)	0.7883 (12)	0.0415 (7)	0.3715 (7)		O(W1)	0.892 (4)	0.054 (3)	0.154 (2)	4.1 (9)
	0.7881 (5)	0.0415 (4)	0.3729 (4)			0.8890 (12)	0.0527 (8)	0.1514 (8)	3.06 (23)
O(11)	0.665 (4)	0.033 (3)	0.374 (2)	3.7 (8)	H(11)	0.846 (2)	0.051 (2)	0.203 (1)	
	0.6620 (10)	0.0323 (7)	0.3713 (6)	2.76 (20)	H(12)	0.838 (2)	0.075 (2)	0.118 (1)	
O(12)	0.852 (4)	−0.033 (2)	0.365 (2)	3.5 (8)	O(W2)	0.057 (3)	0.301 (2)	0.093 (2)	2.4 (6)
	0.8463 (11)	−0.0296 (8)	0.3642 (7)	3.46 (24)		0.0474 (14)	0.3010 (10)	0.0918 (9)	3.96 (28)
O(13)	0.838 (5)	0.079 (3)	0.441 (3)	5.7 (12)	H(21)	0.004 (3)	0.342 (2)	0.090 (2)	
	0.8245 (12)	0.0787 (8)	0.4415 (8)	3.85 (26)	H(22)	0.019 (3)	0.275 (2)	0.057 (2)	
O(14)	0.829 (4)	0.093 (3)	0.310 (2)	3.9 (9)	O(W3)	0.772 (4)	0.269 (2)	0.032 (2)	2.7 (7)
	0.8255 (12)	0.0934 (9)	0.3095 (8)	4.40 (29)		0.7817 (13)	0.2672 (10)	0.0357 (8)	3.39 (25)
Cl(2)	0.6673 (10)	0.2743 (7)	0.4545 (6)		H(31)	0.756 (3)	0.298 (2)	0.069 (2)	
	0.6652 (5)	0.2729 (4)	0.4545 (3)		H(32)	0.745 (3)	0.217 (2)	0.047 (2)	
O(21)	0.774 (4)	0.243 (2)	0.491 (2)	2.6 (7)	O(W4)	0.432 (3)	0.104 (2)	0.472 (2)	2.4 (6)
	0.7672 (10)	0.2413 (7)	0.4954 (6)	2.42 (19)		0.4287 (13)	0.1039 (7)	0.4731 (7)	2.59 (20)
O(22)	0.697 (4)	0.349 (3)	0.427 (2)	4.0 (8)	H(41)	0.501 (2)	0.101 (1)	0.500 (2)	
	0.6943 (10)	0.3485 (7)	0.4267 (7)	3.17 (23)	H(42)	0.366 (2)	0.102 (1)	0.508 (1)	
O(23)	0.637 (3)	0.222 (2)	0.390 (2)	2.2 (6)	O(W5)	0.667 (4)	0.212 (3)	0.225 (2)	5.0 (10)
	0.6330 (10)	0.2190 (7)	0.3953 (6)	2.56 (20)		0.6529 (13)	0.2132 (9)	0.2248 (9)	3.83 (27)
O(24)	0.558 (3)	0.280 (2)	0.506 (2)	2.3 (6)	H(51)	0.693 (3)	0.205 (2)	0.264 (2)	7.5 (8)
	0.5612 (9)	0.2786 (6)	0.5071 (6)	2.18 (18)	H(52)	0.664 (3)	0.271 (2)	0.223 (2)	8.5 (8)
Cl(3)	0.8937 (11)	0.3655 (6)	0.2940 (6)		O(W6)	0.144 (4)	0.405 (2)	0.436 (2)	2.9 (7)
	0.8951 (5)	0.3644 (3)	0.2941 (3)			0.1366 (11)	0.4018 (7)	0.4338 (6)	2.25 (19)
O(31)	0.895 (3)	0.286 (2)	0.326 (2)	2.5 (6)	H(61)	0.208 (2)	0.409 (2)	0.467 (2)	
	0.8992 (10)	0.2853 (7)	0.3261 (6)	2.63 (20)	H(62)	0.132 (2)	0.450 (2)	0.406 (1)	
O(32)	0.788 (3)	0.372 (2)	0.248 (2)	2.4 (6)	O(W7)	0.719 (5)	0.102 (3)	0.039 (2)	4.7 (10)
	0.7877 (10)	0.3710 (7)	0.2479 (6)	2.70 (20)		0.7235 (18)	0.0981 (10)	0.0411 (9)	4.30 (32)
O(33)	0.893 (3)	0.420 (2)	0.354 (2)	2.8 (7)	H(71)	0.650 (2)	0.072 (2)	0.042 (2)	
	0.8943 (10)	0.4214 (7)	0.3538 (6)	2.62 (20)	H(72)	0.756 (3)	0.097 (2)	−0.006 (2)	

[a] Numbering of atoms: the oxygen atom O(*pqr*) is the one bonded to the bismuth atoms Bi(*p*), Bi(*q*), and Bi(*r*); the hydrogen atom H(*pqr*) is bonded to the oxygen atom O(*pqr*); the oxygen atom O(*st*) is the *t*th one bonded to the chlorine atom Cl(*s*); the hydrogen atom H(*uv*) is the *v*th one bonded to the water oxygen O(W*u*).

hydroxide $Sn_6O_4(HO)_4$ and possibly an isostructural lead hydroxide by Howie and Moser.[29] In these structures all metal–oxygen distances are reported to be of equal length, i.e. a regular cubic arrangement of the oxygens around the metal octahedron. The uranium and cerium salts were investigated by film methods; hence, the oxygen positions are uncertain (in the uranium salt determined by geometrical arguments). The communication describing the tin compound gives no information about the atomic parameters, only the interatomic distances. It is thus impossible to assess the accuracy of the oxygen positions.

Aurivillius and co-workers have determined the structures of a number of bismuth salts, among them the basic salts $BiHOCrO_4$[30,31] (monoclinic and orthorhombic), $Bi_2O_2SO_4\cdot$

---

(29) R. A. Howie and W. Moser, *Nature* (*London*), **219**, 372 (1968).

(30) B. Aurivillius and I. Jonsson, *Ark. Kemi*, **19**, 271 (1962).

Table III. Selected Interatomic Distances[a] (Å) Based on Neutron Data in the Complex $Bi_6O_4(HO)_4^{6+}$ with Their Estimated Standard Deviations (in Parentheses)

Bi-Bi		Bi-O			
		oxide oxygens		hydroxide oxygens	
Bi(1)-Bi(2)	3.707 (8)	O(124)-Bi(1)	2.171 (10)	O(125)-Bi(1)	2.478 (11)
Bi(1)-Bi(4)	3.655 (8)	O(124)-Bi(2)	2.142 (10)	O(125)-Bi(2)	2.390 (11)
Bi(1)-Bi(5)	3.726 (8)	O(124)-Bi(4)	2.158 (10)	O(125)-Bi(5)	2.415 (11)
Bi(1)-Bi(6)	3.646 (8)	O(156)-Bi(1)	2.135 (10)	O(146)-Bi(1)	2.293 (11)
Bi(2)-Bi(3)	3.705 (8)	O(156)-Bi(5)	2.172 (10)	O(146)-Bi(4)	2.443 (11)
Bi(2)-Bi(4)	3.641 (9)	O(156)-Bi(6)	2.144 (10)	O(146)-Bi(6)	2.479 (11)
Bi(2)-Bi(5)	3.633 (8)	O(235)-Bi(2)	2.139 (10)	O(234)-Bi(2)	2.386 (10)
Bi(3)-Bi(4)	3.633 (8)	O(235)-Bi(3)	2.197 (10)	O(234)-Bi(3)	2.409 (10)
Bi(3)-Bi(5)	3.655 (8)	O(235)-Bi(5)	2.100 (10)	O(234)-Bi(4)	2.348 (10)
Bi(3)-Bi(6)	3.677 (8)	O(346)-Bi(3)	2.108 (10)	O(356)-Bi(3)	2.396 (11)
Bi(4)-Bi(6)	3.764 (8)	O(346)-Bi(4)	2.185 (10)	O(356)-Bi(5)	2.385 (12)
Bi(5)-Bi(6)	3.653 (9)	O(346)-Bi(6)	2.195 (10)	O(356)-Bi(6)	2.396 (11)
mean	3.675	mean	2.154	mean	2.402

[a] The O-H distances are listed in Table V.

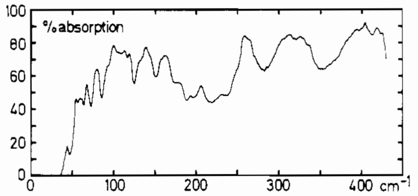

Figure 3. Low-frequency infrared spectrum of polycrystalline $Bi_6O_4(HO)_4(ClO_4)_6{\cdot}7H_2O$ at 100 K.

H_2O,[32] and $BiHOSeO_4{\cdot}H_2O$.[32] The endless sheets, consisting of BiO^+ or $Bi_2O_2^{2+}$ units with equal Bi- - -Bi distances throughout the layers, found in the bismuth oxide halides (Bannister and Hey,[33] Sillén,[34] Aurivillius[35]) have in these structures been split to recognizable dinuclear, doubly oxygen-bridged square complexes $Bi_2O_2^{2+}$, $Bi_2O(HO)^{3+}$, or $Bi_2(HO)_2^{4+}$.

The Bi- - -Bi distances in the dinuclear aggregates in these structures vary between 3.664 (3) and 3.684 (4) Å, which is in fair agreement with the mean Bi- - -Bi distance of 3.68 (4) Å (the number in parentheses is the estimated standard deviation of the mean from the individual values) (both X-rays and neutrons) in the present complex.

The differences between the different Bi- - -O distances in the dinuclear complexes give no evident indication of whether the bridging oxygens in these complexes are of the oxide or the hydroxide type. The distances in the dinuclear complexes vary between 2.09 (9) and 2.30 (3) Å,[36] which is within the range of Bi- - -O distances formed in the hexanuclear complex.

Bismuth–Oxygen Coordination. The trigonal bipyramid is a common coordination polyhedron in compounds of elements having a stereoactive lone ns^2 pair, the lone pair filling the role of the fifth ligand at one of the equatorial apexes, where it occupies approximately the same space as an anion.[37–40]

As distinguished from the square-pyramidal coordination of oxygen to Bi in the BiOCl structure,[41] the trigonal-bipyramidal coordination geometry can be recognized in the $Bi_6O_4(HO)_4^{6+}$ complex, each bismuth bonding two equatorial oxide oxygens and two axial hydroxide oxygens and thus having the long pair pointing radially out from the Bi_6 cage. The equatorial Bi- - -O^{2-} distances are significantly shorter (mean value 2.15 (3) Å) than the axial Bi- - -OH^- distances (mean value 2.40 (5) Å). The O^{2-}- - -Bi- - -O^{2-} angles vary between 88.8 (4) and 91.3 (4)° (mean value 90.3 (10)°), and the HO^-- - -Bi- - -OH^- angles vary between 124.8 (4) and 127.7 (4)° (mean value 126.4 (10)°). In the BiOCl type structures all O- - -Bi- - -O angles in the square-pyramidal coordination polyhedron are equal and are about 116°.

The average distances for the equatorial–equatorial and the equatorial–axial oxygens are 3.05 (3) and 2.67 (2) Å, respectively. The ratio of these distances is 1.14, in fair agreement with the average value of 1.05 (no estimated error given) reported by Galy et al.,[40] the discrepancy probably being insignificant. The steric hindrance exerted by the Bi octahedron on the equatorial oxygens may, however, result in a slight elongation of the equatorial–equatorial distances.

According to Galy et al.,[40] the two ligands and the center of the lone pair (E) in the equatorial plane should form an equilateral triangle; hence, the Bi- - -(E) distances can easily be calculated.[39] The values obtained vary between 1.02 and 1.18 Å, which may be compared with the mean Sb- - -(E) value of 1.1 (±0.3) Å calculated from 17 structures by Bovin[39] and with the single value of 0.98 Å calculated for the Bi- - -(E) distance in $Bi_2Ti_4O_{11}$.[40]

Each bismuth is weakly coordinated to four other oxygens in perchlorate groups or water molecules situated outside the complex. These bond distances are fairly long and fall in the range 2.61 (1)–3.00 (1) Å; i.e., Bi is surrounded by a total of eight oxygen atoms. The geometric arrangements are all different and irregular and could be described as very distorted bicapped trigonal prisms or dodecahedra.

As the O- - -O distances for the outer oxygen atoms are considerably longer than those in the complex, space is left for the inert $6s^2$ pair. The coordinates for the centers of the lone pairs were calculated by using the model of Galy et al. In this way it is possible to calculate the contact distances between the lone pairs and the outer oxygens. In all cases but one, these distances (2.21–2.84 Å) are compatible with published data in other structures, the exception being Bi(5), where the distance (E)- - -O(44) is only 1.90 Å. In this case, the lone pair may be twisted out of the ideal position.

Comparison with Vibrational Spectra. Maroni and Spiro[5] used an idealized O_h symmetry when interpreting the infrared and Raman spectra of solids and solutions containing the hexanuclear bismuth complex. This choice was based on the

---

(31) B. Aurivillius and A. Löwenhielm, *Acta Chem. Scand.*, **18**, 1937 (1964).
(32) B. Aurivillius, *Acta Chem. Scand.*, **18**, 2375 (1964).
(33) F. A. Bannister and M. H. Hey, *Mineral. Mag.*, No. **149**, 49 (1935). **149**, 49 (1935).
(34) L. G. Sillén, *Naturwissenschaften* **30**, 318 (1942).
(35) B. Aurivillius, *Acta Chem. Scand.*, **18**, 1823 (1954).
(36) Recalculation of the interatomic distances in the sulfate and selenate structures gave slight differences (at most 0.04 Å) from the values given by Aurivillius et al.
(37) R. J. Gillespie and R. S. Nyholm, *Q. Rev. Chem. Soc.*, **11**, 339 (1957).
(38) R. J. Gillespie in "Inorganic Chemistry", Van Nostrand-Reinhold, London, 1972.
(39) J.-O. Bovin, Thesis, University of Lund, Lund, Sweden, 1975.
(40) J. Galy, G. Meunier, S. Andersson, and A. Åström, *J. Solid State Chem.*, **13**, 142 (1975).
(41) L. G. Sillén, *Sven. Kem. Tidskr.*, **53**, 39 (1941).

Table IV. Raman and Infrared Frequencies Attributable to the $Bi_6O_4(HO)_4{}^{6+}$ Complex[a]

Raman		far-infrared	Raman[f]		infrared[f]
solid	soln	solid	solid	soln	solid
92 (vs)	87 (s)	91[b] (s)	90	88	?
109 (vs)	104 (s)	106[e] (vw)	108	107	?
150 (m)	~150[b]	157[b] (s)	~147	148	?
186 (vs)	178 (vs, p)	181[b] (w) 192 (w)	187	177	
262 (w)		258 (vs) 264[b] (vs)	263	258	263
292[e] (vw)		285 (vw) 312[c] (vs)			
326 (w)	335[c] (w)	326 (vs)		340[e]	325
407[b] (w) 441 (m) 446 (m) 456 (m)	441–450[d] (p)	404 (vs)	407	(407)[b]	406
			440	(435)[b]	434
			451	~447 (p)	
					571

[a] vs = very strong, s = strong, w = weak, vw = very weak, and p = polarized. [b] Not resolved; shoulder. [c] Very broad. [d] Broad shoulder. [e] Uncertain. [f] From measurements in ref 5.

structure suggested by Levy et al.,[4] but neglecting the hydrogen atoms. In O_h symmetry there should be eight Raman-active and four infrared-active fundamentals with no coincidences. The ideal symmetry of the $Bi_6O_4(HO)_4{}^{6+}$ complex, still neglecting the hydrogen atoms, is T_d. After subtraction of the representations corresponding to translation, rotation, and infrared- and Raman-inactive vibrations, there remain $\Gamma_{vib} = 3\ A_1 + 3\ E + 6\ T_2$ or six infrared-active and twelve Raman-active fundamentals with full coincidence.

The Raman spectra of the basic perchlorate in solid and in solution were redetermined. The low-frequency infrared spectrum at 100 K of the solid (Figure 3) was also studied. The experimental results are given in Table IV and show ten, or perhaps eleven, Raman frequencies attributable to the Bi_6 complex. Further, the ν_2 band at 471 cm^{-1} (solid) and 462 cm^{-1} (solution) of free perchlorate was observed, in addition to a weak band at 220 cm^{-1}, which is most probably a "laser line". The far-infrared region is expected to contain a number of bands caused by lattice vibrations, site-symmetry-allowed vibrations, and translational vibrations of water molecules, etc. Out of the about 25 (including unresolved) bands found in the region 40–420 cm^{-1}, only those of interest for the following discussion are listed.

The Raman spectrum of the solution contains a broad shoulder on the 432-cm^{-1} perchlorate band. In the spectrum of the solid, this shoulder is resolved into distinct bands. Maroni and Spiro reported three bands, of which the 440-cm^{-1} band was rather broad. As considerable polarization of the shoulder was observed, they concluded that at least one of the bands should be totally symmetric and assigned the 447-cm^{-1} band to one of the two predicted A_{1g} fundamentals. The other one was the polarized 177-cm^{-1} band.

In the present spectrum of the solid, the 440-cm^{-1} band is further resolved into two bands at 441 and 446 cm^{-1}. There is no experimental evidence for assuming that only the 447-cm^{-1} band is polarized. Any two of the bands hidden in the shoulder could be polarized and correspond to two of the three predicted A_{1g} fundamentals of the T_d molecule $Bi_6O_4(HO)_4{}^{6+}$, the third being the 178-cm^{-1} band.

Maroni and Spiro reported a band at 340 cm^{-1} in the solution spectrum (the band seems in fact to be nearer 330 cm^{-1} as judged by Figure 1a in their paper). This band is in good agreement with the weak bands at 325 cm^{-1} (solid) and 335 cm^{-1} (solution) found in this study. A corresponding band at 325 cm^{-1} was found in the IR spectrum of the solid.

The low-frequency infrared spectrum (Figure 3) is in agreement with the results in ref 5, the 263-cm^{-1} IR band in ref 5 possibly being resolved into the two frequencies 258 and 254 cm^{-1}. Due to the great number of frequencies in the region below 200 cm^{-1}, it is not easy to interpret this part of the spectrum. The distortion of the complex is likely to result in more frequencies than the six expected for the ideal T_d symmetry, some of which may lie in the far-infrared region. As mentioned earlier, this region also contains absorptions due to lattice vibrations etc. However, there is at least one frequency (at 91 cm^{-1}) that most certainly coincides with a Raman band (at 92 cm^{-1}, solid).

We can now compare the O_h and the T_d models with experimental data. There is virtually a full coincidence between infrared and Raman frequencies, with due regard to the fact that there should be twice as many Raman as IR frequencies in the ideal case. This is in direct violation of the exclusion principle, valid for O_h symmetry. Maroni and Spiro explained the disagreement between the O_h model and experiment as a result of a trigonal distortion to D_3 symmetry. The O_h model would give six Raman bands; Maroni and Spiro reported seven. The "extra" band at 340 cm^{-1} was assumed to be due to an interaction between complex and solvent water. In a following paper,[6] Maroni and Spiro reported a normal-coordinate analysis of the $Bi_6(HO)_{12}{}^{6+}$ complex that failed to explain the 148-cm^{-1} Raman band. This was then assumed to be an instrumental artifact. The present investigation, however, confirms the presence of the 148-cm^{-1} band.

In our opinion, the spectroscopic data of Maroni and Spiro show that the model they used for the bismuth hydroxide complex is not correct, and the reexamined spectra give further support to this conclusion. At least ten frequencies attributable to the twelve predicted Raman-active fundamentals of the T_d model were found, and there is full coincidence with infrared data (Table IV). Thus, the T_d model of the $Bi_6O_4(HO)_4{}^{6+}$

Table V. Hydrogen Bond System with Estimated Standard Deviations in Parentheses

	O–H, Å		H···O, Å		O–O, Å	
atoms	uncor	riding motion	uncor	independent	uncor	O–H···O, deg
O(125)–H(125)···O(34)	0.96 (2)	0.99 (2)	2.15 (2)	2.18 (2)	2.96 (2)	142 (2)
O(146)–H(146)···O(W6)	0.97 (2)	0.99 (2)	1.76 (2)	1.79 (2)	2.73 (2)	177 (2)
O(234)–H(234)···O(W3)	1.01 (2)	1.03 (2)	1.74 (2)	1.78 (2)	2.74 (2)	178 (2)
O(356)–H(356)···O(11)	0.96 (2)	0.98 (2)	1.78 (2)	1.82 (2)	2.72 (2)	169 (2)
O(W1)–H(11)···O(14)	1.01 (3)	1.05 (3)	2.01 (3)	2.07 (3)	2.92 (2)	149 (2)
O(W1)–H(12)···O(W7)	0.90 (3)	0.93 (3)	1.88 (3)	1.94 (3)	2.76 (2)	167 (3)
O(W2)–H(21)···O(51)	0.85 (4)	1.02 (4)	2.26 (4)	2.36 (4)	3.09 (2)	166 (4)
O(W3)–H(32)···O(W7)	0.96 (4)	1.02 (4)	2.04 (4)	2.11 (4)	2.95 (2)	157 (3)
O(W4)–H(41)···O(W6)	0.93 (3)	0.97 (3)	1.89 (3)	1.94 (3)	2.82 (2)	172 (2)
O(W4)–H(42)···O(22)	0.93 (3)	0.97 (3)	2.36 (3)	2.41 (2)	3.23 (2)	155 (2)
O(W5)–H(52)···O(32)	0.99 (4)	1.05 (4)	2.23 (4)	2.29 (4)	3.10 (2)	146 (3)
O(W6)–H(61)···O(13)	0.98 (3)	1.05 (3)	2.06 (3)	2.12 (3)	3.03 (2)	166 (2)
O(W6)–H(62)···O(W1)	0.95 (3)	0.98 (3)	2.03 (3)	2.08 (3)	2.97 (2)	177 (2)
O(W7)–H(71)···O(53)	0.93 (3)	0.97 (3)	2.23 (3)	2.29 (3)	3.04 (2)	145 (2)
O(W7)–H(72)···O(43)	0.89 (4)	0.93 (4)	2.15 (3)	2.21 (3)	2.97 (2)	152 (3)

complex is certainly in better agreement with the experimental data than the O_h model.

Maroni and Spiro found in their normal-coordinate analysis that the calculated frequencies were not very sensitive to uncertainties in the oxygen positions but that a much better fit to the observed spectra was obtained when a valence force between the bismuth atoms was introduced. Maroni and Spiro discussed[6,42] whether this effect could be attributed to metal–metal bonding and gave some experimental evidence for a bonding of this type. However, the Bi- - -Bi distance is much longer in the complex, 3.68 Å, than the Bi- - -Bi distance in the metal, 3.10 Å. The Bi- - -Bi distance in the $Bi_6O_4(HO)_4^{6+}$ molecule agrees well with the distances found in the dinuclear complexes, where there is no reason to suspect any metal–metal bonding. Furthermore, in the true metal cluster Bi_9^{5+}, which has been found in the subchloride $Bi_{24}Cl_{28}$[43] and the compound $Bi^+Bi_9^{5+}(HfCl_6^{2-})_3$,[44] the Bi- - -Bi distances lie in the range 3.08–3.29 Å. It seems improbable that bismuth would have any metal–metal bonding at all at the considerably longer distance in the hexanuclear complex.

The Hydrogen Bonds and the Water Molecules. Correction for thermal motion was performed by using the riding-motion model for the O- - -H bonds and with the assumption of independent motions of the atoms in the O···H interactions. As a check, the riding-motion model, though less adequate, was also tried. Both models gave the same bond distances within two estimated standard deviations. For the very short O- - -H bonds, the corrections were quite large. The shortest uncorrected O- - -H distance (O(W2)- - -H(22)) was elongated from 0.82 (4) to 0.94 (4) Å.

According to Olovsson and Jönsson,[45] the limiting O···H distance in a hydrogen bond can be taken as 2.4 Å. In the present structure, acceptor atoms at distances below this limit can be found for all the hydrogen atoms but three. Judging from the O···H distances, most of the H-bond interactions must, however, be considered to be very weak. The distances and angles in the hydrogen-bond system are summarized in Table V.

All the HO^- groups in the complex are hydrogen bonded with relatively short O···H distances. Three of the H bonds are nearly linear, while the fourth is bent. In the latter case, the hydrogen atom H(125) may participate in a bifurcated hydrogen bond as there is an additional oxygen O(12) at a rather close distance of 2.60 Å (corrected value, independent motion) and an angle of 139 (1)°. The three hydrogen atoms H(22), H(31), and H(51), which are considered not to be H bonded, still have several close oxygen atoms. The distances and angles seem, however, to rule out any hydrogen-bond interaction.

The large estimated standard deviations do not justify a detailed discussion of the bond lengths in the hydrogen-bond system. As can be seen from Table V, no correlation can be found between the O- - -H and the O···H or O- - -O distances, possibly a result of the large experimental errors.

The Perchlorate Groups. The perchlorate groups are close to tetrahedral, only three of the O- - -Cl- - -O angles deviating from the tetrahedral angle (at most 4.7°). The Cl- - -O bond lengths, corrected for riding motion, vary between 1.39 (1) and 1.51 (2) Å with a mean of 1.44 Å. Berglund, Thomas, and Tellgren give an average of 1.426 Å for Cl- - -O in both an X-ray[46] and a neutron diffraction[47] study of $NaClO_4 \cdot H_2O$, while Sequeira, Bernal, Brown, and Faggiani[48] found the two crystallographic independent Cl- - -O distances 1.460 (2) and 1.456 (2) Å (corrected for riding motion) in the completely regular ClO_4^- ion in $Li(H_2O)_3ClO_4$. No obvious correlation between the differences in the Cl- - -O distances and the different coordination or hydrogen-bond situations at the oxygen atoms could be found.

Acknowledgment. I am greatly indebted to Professor Ingmar Grenthe and Dr. Georg Johansson of this institute for their helpful advice and for many valuable discussions on the manuscript. Dr. Roland Tellgren, who assisted with the neutron data collection, Dr. Jan-Olov Lundgren, who helped with computing problems, and Dr. Jan Lindgren, who collected the low-frequency infrared spectrum, all of the University of Uppsala, are also thanked for their generous support. I also thank Dr. Magnus Sandström of this institute for his kind interest in the work and for collecting the Raman spectra. This work has been financially supported by the Swedish Natural Science Research Council and by the foundation "Knut & Alice Wallenbergs Stiftelse".

Registry No. $Bi_6O_4(OH)_4(ClO_4)_6 \cdot 7H_2O$, 85507-36-4.

Supplementary Material Available: Listings of observed and calculated structure factors, anisotropic thermal parameters for the Bi, Cl, and H atoms (Table IIb), and bonding parameters for the perchlorate ions (43 pages). Ordering information is given on any current masthead page.

---

(42) T. G. Spiro, in *Prog. Inorg. Chem.* **11** (1970).

(43) A. Hershaft and J. D. Corbett, *Inorg. Chem.*, **2**, 979 (1963).

(44) R. M. Friedman and J. D. Corbett, *Inorg. Chem.*, **7**, 198 (1968).

(45) I. Olovsson and P. G. Jönsson in "The Hydrogen Bond—Recent Developments in Theory and Experiments", Vol. II, P. Schuster et al., Eds., North-Holland Publishing Co., Amsterdam, 1976, pp 395–456.

(46) B. Berglund, J. O. Thomas, and R. Tellgren, *Acta Crystallogr., Sect. B*, **B31**, 1842 (1975).

(47) B. Berglund, R. Tellgren, and J. O. Thomas, *Acta Crystallogr., Sect. B*, **B32**, 2444 (1976).

(48) A. Sequeira, I. Bernal, I. D. Brown, and R. Faggiani, *Acta Crystallogr., Sect. B*, **B31**, 1735 (1975).