*Contribution from the Department of Chemistry,
Rice University, Houston, Texas 77001, U.S.A.*

# High Pressure - High Temperature Syntheses.[*] I.
# The Preparation of Mercury Metaborate, $Hg_4O(BO_2)_6$

**C. H. Chang and J. L. Margrave**

*Received July 20, 1967*

*Mercury metaborate has been synthesized in a tetrahedral anvil press at pressures of 24 to 40 kilobars and temperatures from 700 to 940°C. The new metaborate, isostructural with zinc metaborate, has a cubic lattice with $a = 7.56 \pm 0.02$ Å. The tetrahedral coordination around boron in this compound is established by the infrared absorption spectrum. The borate decomposes in a stream of $H_2$ at 360°C and both $\alpha$–$B_2O_3$ and $\beta$–$B_2O_3$ are formed during the decomposition. $Hg_4O(BO_2)_6$ is more stable than mercuric oxide and decomposes at 565°C under vacuum.*

## Introduction

Anhydrous metal borates have received considerable attention from chemists and many borates have been reported to exist. In most borates, the boron atoms are in the centers of triangles, surrounded by three equivalent oxygen atoms; but boron can have coordination numbers 3 and 4 at the same time in some borates. There are only a few known borates which contain only tetrahedrally-coordinated borons.

In Group IIb, zinc has been reported to form the metaborate, $Zn_4O(BO_2)_6$, in which all of the boron atoms have coordination number 4. $Zn_4O(BO_2)_6$ crystallizes in a cubic structure,[1,2] with $a = 7.49 \pm 0.06$ Å and space group $Td^3$–I43m. It has strong absorption bands in the region 800 to 1100 cm.$^{-1}$, characteristic of 4-fold coordination of boron.[3,4]

Mercuric oxide, HgO, is stable only up to 400°C[5] at atmospheric pressure and no corresponding mercury metaborate has been reported. From a thermal decomposition study of HgO,[6] it has been found possible to retain HgO even up to ~1000°C under high pressures. Furthermore, the increase in pressure favors higher coordination numbers.[7] It is, therefore, reasonable to speculate that a mercury metaborate, isostructural with $Zn_4O(BO_2)_6$, can be synthesized under high pressures and high temperature.

## Experimental Section

The tetrahedral anvil[8,9] was used for this study. The pressure scale was calibrated at the $Bi^{I-II}$, $Bi^{II-III}$ and $Tl^{II-III}$ transitions and temperatures were measured by inserting a Pt—Pt +10% Rh thermocouple into the sample container through edges of the tetrahedron.[6]

Boric oxide, $B_2O_3$, was obtained from U. S. Borax and dried at 170°C for more than 24 hours before being used. A 1:1 molar mixture of $B_2O_3$ and reagent grade yellow HgO (Merck and Co., Inc.) was prepared in the dry box and transfered into the tetrahedral high pressure cell, with BN as the container. Pressures used for the reaction ranged from 24 to 32 kilobars and temperatures from 700 to 800°C. After the mixture was kept under high pressure and high temperature for a period of 40 hours, the heating current was shut off and the whole system was cooled by a blast of cool air in a few seconds. The pressure was then released in one minute. The yellow product obtained was then heated in an $H_2$ stream at 250°C for 5 hours to give a black product, mercury metaborate. When a 2:1 molar mixture of purified BN powder (Fisher) and HgO was heated at 40 kilobars and 940°C in a BN-container with a graphite heater for 8 hours, the black mercury metaborate was obtained after quenching.

Excess HgO was decomposed and removed in a $H_2$-stream at 250°C to prevent the decomposition of mercury metaborate and unreacted $B_2O_3$ was dissolved in hot water. Liquid mercury formed in the reaction was "distilled" in vacuum at 160°C and condensed at liquid $N_2$-temperature.

## Results and Discussion

Quenched mercury metaborate is black in color. The Debye-Scherrer powder photograph was taken at room temperature in a Norelco 114.6-m.m. camera with Ni-filtered $CuK_\alpha$ radiation at 35 kV and 18 mA for 4 hours. The diffraction pattern could be indexed on a cubic lattice structure with $a = 7.56 \pm 0.02$ Å. The Miller indices and relative intensities confirm that mercury metaborate is indeed isostructural with cubic zinc metaborate. Table I shows the results of indexing and a comparison with the diffraction pattern of zinc

---

(*) Extracted, in part, from the Ph. D. thesis of C. H. Chang, submitted to the faculty of Rice University, May (1967).

(1) P. Smith, S. Garcia-Blanco and L. Rivoir, *Z. Krist.*, *115*, 460 (1961).

(2) S. Terol, M. J. Ottero de la Gandard, *An. Soc. Esp. Fisica y Quim.*, 57 (B), 343 (1961).

(3) J. Krogh-Moe, *Z. Krist.*, *117*, 116 (1962).

(4) C. E. Weir and R. A. Schroeder, *J. Research NBS*, *68A*, 465 (1964).

(5) D. Taylor, *J. Chem. Soc.*, 1047 (1962).

(6) C. H. Chang, Ph. D. Thesis, Rice University (1967).

(7) See for example, M. L. Huggins, p. 238, «Phase Transformations in Solids», edited by R. Smoluchoski and J. E. Mayer, J. Wiley, New York.

(8) H. T. Hall, *Rev. Sci. Inst.*, *29*, 267 (1958).

(9) H. T. Hall, «High Pressure-Temperature Apparatus» in «Metallurgy at High Pressures and High Temperatures», edited by K. A. Gscheidner J., M. T. Hepworth and N. A. D. Parlee, Gordon and Breach Science Publishers, New York (1964).

metaborate. The cell constant of the new mercury borate is quite reasonable when compared with that of isostructural zinc borate if one considers the relative sizes of the Hg$^{II}$ and Zn$^{II}$ ions.

**Table I.** X-ray Diffraction Patterns for Mercury and Zinc Metaborates

| Relative Intensity | d | hkl | a |
|---|---|---|---|
| | Mercury Metaborate | | |
| M[a] | 5.30 | 110 | 7.50 |
| S | 3.08 | 211 | 7.54 |
| S | 2.39 | 310 | 7.56 |
| M | 2.18 | 222 | 7.55 |
| S | 2.02 | 321 | 7.56 |
| W | 1.890 | 400 | 7.57 |
| S | 1.781 | 411 | 7.56 |
| W | 1.671 | 332 | 7.58 |
| M | 1.483[b] | 510 | 7.56 |
| W | 1.380 | 521 | 7.56 |
| W | 1.341 | 440 | 7.58 |
| W | 1.302 | 530 | 7.59 |
| M | 1.233 | 611 | 7.60 |
| VW | 1.171 | 541 | 7.59 |
| W | 1.146 | 622 | 7.60 |
| W | 1.121 | 631 | 7.60 |
| W | 1.030 | 721 | 7.57 |
| W | 0.994 | 730 | 7.57 |
| M | 0.962 | 732 | 7.57 |
| M | 0.933 | 811 | 7.58 |
| W | 0.906 | 653 | 7.58 |
| S | 0.882 | 830 | 7.54 |
| M | 0.870 | 751 | 7.54 |
| W | 0.859 | 832 | 7.54 |
| W | 0.848 | 840 | 7.58 |
| VW | 0.838 | 900 | 7.54 |
| S | 0.818 | 920 | 7.54 |
| S | 0.800 | 922 | 7.55 |
| S | 0.783 | 852 | 7.55 |
| S | 0.775 | 932 | 7.51 |
| a = 7.56±0.02 Å | | | |
| | Zinc Metaborate[c] | | |
| 2 | 5.43 | 110 | 7.68 |
| 1 | 3.76 | 200 | 7.52 |
| 100 | 3.05 | 211 | 7.47 |
| 11 | 2.36 | 310 | 7.46 |
| 1 | 2.16 | 222 | 7.48 |
| 10 | 1.995 | 321 | 7.47 |
| 5 | 1.868 | 400 | 7.47 |
| 20 | 1.761 | 411 | 7.47 |
| 3 | 1.672 | 420 | 7.48 |
| 1 | 1.593 | 332 | 7.47 |
| 4 | 1.525 | 422 | 7.47 |
| 4 | 1.465 | 510 | 7.47 |
| 5 | 1.364 | 521 | 7.47 |
| a = 7.49±0.06 Å | | | |

[a] S, strong; M, medium; W, weak; V, very. [b] Following this line d-values are calculated from $CuK_{\alpha_1}$. [c] Data are taken from P. Smith, S. Garcia-Blanco and L. Rivoir, *Zeitschrift fuer Kristallographie, 115*, 460 (1961).

The infrared absorption spectra of various borates were recorded, (see Figure 1), by using the KBr-disk technique, and a Beckman IR-9 Infrared Spectrophotometer. All of the absorption bands for mercury metaborate are below ~1200 cm.$^{-1}$, indicating that the borons are in 4-fold coordination. The strong bands between 1000-1100 cm.$^{-1}$ are characteristic of 4-fold coordination.

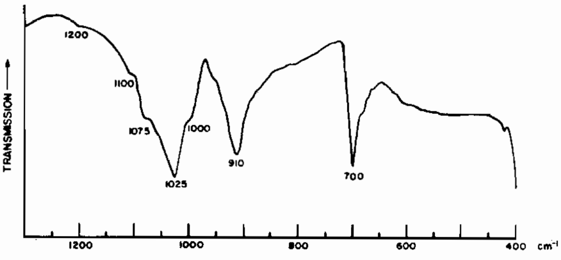

Figure 1. Infrared Spectrum of Mercury Metaborate.

The assignments of the observed bands in Table II, given on the basis of Weir and Schroeder's assignment for zinc metaborate,[4] and assuming effective $C_{3v}$ symmetry for the $BO_4$-group using the terminology of Herzberg,[10] imply $\nu_6 \approx 200 \pm 50$ cm.$^{-1}$.

**Table II.** Infrared Absorption Spectra of Cubic Mercury and Zinc Metaborates

| $Zn_4O(BO_2)_6$[a] | | $Hg_4O(BO_2)_6$ | | Assignment |
|---|---|---|---|---|
| 1200 | WSh[b] | 1200 | WSh[b] | $\nu_1+\nu_6$ |
| 1160 | WSh | 1100<br>1075 | WSh<br>WSh | $(\nu_2+\nu_6)$, or $(\nu_1+\nu_6)$ |
| 1082 | SVB | 1025 | SB | $\nu_5(E)$ |
| 1037 | M | 1000 | M | $\nu_1(A_1)$ |
| 927 | S | 910 | SB | $\nu_2(A_1)$ |
| 717 | S | 700 | S | $\nu_4(E)$ |
| 470 | S | (~400) | | $\nu_3(A_1)$ |

[a] Data from C. E. Weir and R. A. Schroeder, *J. Research N.B.S.*, *68A*, 465 (1964). [b] W, weak; M, medium; S, strong; V, very; B, broad; and Sh, shoulder.

One should note that as the unit cell dimension increases, the absorption frequencies shift to lower frequencies. The behavior parallels that found previously in isostructural divalent metal orthoborates[4] and in isostructural carbonates and nitrates[11] where the shift was attributed to the effect of less anion repulsion in the more loosely packed structure.

A purified sample was introduced into a resistively-heated alumina Knudsen cell in a Bendix Model 14-206a time-of-flight mass spectrometer; at 565°C, both $Hg^+$ and $Hg^{2+}$ were observed, due to the thermal decomposition of the borate. Under high vacuum in the mass spectrometer, pure HgO decomposes at 270°C;[12] thus, the borate is more stable thermally than the oxide.

When mercury metaborate was heated at 360°C for 5 hours in a stream of $H_2$, decomposition occurred and the color changed from black to white. The x-ray diffraction pattern shown in Table III indicates the formation of both $\alpha$– and $\beta$–$B_2O_3$. The formation of some dense $\beta$–$B_2O_3$ from the tetrahedrally-coordinated $Hg_4O(BO_2)_6$ is consistent with the observation of Dachille and Roy[13] who calculated from infrared data on $\beta$–$B_2O_3$ that B has an average coordination number of 3.4, while in $\alpha$–$B_2O_3$ the average coordination number is 3.2.

---

(10) G. Herzberg, Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules, D. Van Nostrand Co., Inc., New York (1949).

(11) C. E. Weir and E. R. Lippincott, *J. Research NBS, 64A*, 103 (1960).

(12) M. Onchi and I. Kusunoki, *Nippon Kagaku Zasshi, 85*, 617 (1964).

(13) F. Dachille and R. Roy, *J. Am. Ceram. Soc., 42*, 78 (1959).

**Table III.** X-ray Diffraction Pattern of Decomposed Mercury Metaborate

| Product | | $\alpha$–$B_2O_3$ [a] | | $\beta$–$B_2O_3$ [b] | | $H_3BO_3$ [a] | |
|---|---|---|---|---|---|---|---|
| Relative Intensity | d | Relative Intensity | d | Relative Intensity | d | Relative Intensity | d |
| W | 6.10 | | | | | 20 | 6.04 |
| M | 33.8 | | | VS | 3.905 | | |
| M | 3.42 | 50 | 3.42 | | | | |
| W | 3.20 | | | | | 100 | 3.18 |
| M | 2.85 | | | VS | 2.865 | | |
| S | 2.78 | 90 | 2.78 | | | | |
| M | 2.23 | 70 | 2.23 | | | | |
| S | 2.10 | 100 | 2.096 | | | | |
| VW | 2.06 | | | | | 6 | 2.08 |
| W | 1.98 | | | M | 1.987 | | |
| VW | 1.92 | 20 | 1.920 | | | | |
| W | 1.82 | 20 | 1.822 | | | | |
| VW | 1.79 | | | W | 1.789 | | |
| W | 1.71 | 50 | 1.710 | | | | |
| VW | 1.40 | 50 | 1.403 | | | | |
| VW | 1.20 | 50 | 1.197 | | | | |

[a] Data taken from ASTM cards. [b] Data taken from Dachille and Roy, *J. Am. Ceram. Soc.*, *42*, 78 (1959).

## Conclusions

The preparation of cubic mercury metaborate has been accomplished as follows:

$$(1)\quad 2HgO + B_2O_3 \xrightarrow[770°C,\,40\,hrs]{30\ Kbar} \text{yellow product} \xrightarrow[250°C,\,5\,hrs]{H_2}$$

$$\frac{1}{3}\,[Hg_4O(BO_2)_6] + \frac{2}{3}\,Hg + \frac{2}{3}\,H_2O$$

$$(2)\quad 13HgO + 6BN \xrightarrow[940°C,\,10\,hrs]{40\ Kbar}$$

$$Hg_4O(BO_2)_6 + 9Hg + 3N_2$$

*Acknowledgments.* This work was supported financially by the U. S. Army Research Office, Durham, North Carolina. The authors wish to express their appreciation to Dr. P. Ficalora for his technical assistance.