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

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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±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 α–B_2O_3 and β–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± 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_α 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±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 Jr., M. T. Hepworth and N. A. D. Parlee, Gordon and Breach Science Publishers, New York (1964).

etaborate. The cell constant of the new mercury orate is quite reasonable when compared with that of ostructural zinc borate if one considers the relative zes of the Hg^{II} and Zn^{II} ions.

able I. X-ray Diffraction Patterns for Mercury and Zinc etaborates

elative tensity	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
= 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
= 7.49±0.06 Å			

, strong; M, medium; W, weak; V, very. [b] Following line d-values are calculated from CuK_{α_1}. [c] Data are taken m P. Smith, S. Garcia-Blanco and L. Rivoir, *Zeitschrift fuer ristallographie, 115,* 460 (1961).

The infrared absorption spectra of various borates re recorded, (see Figure 1), by using the KBr-disk hnique, and a Beckman IR-9 Infrared Spectrophotoeter. All of the absorption bands for mercury metarate are below ~1200 cm.$^{-1}$, indicating that the ons are in 4-fold coordination. The strong bands tween 1000-1100 cm.$^{-1}$ are characteristic of 4-fold ordination.

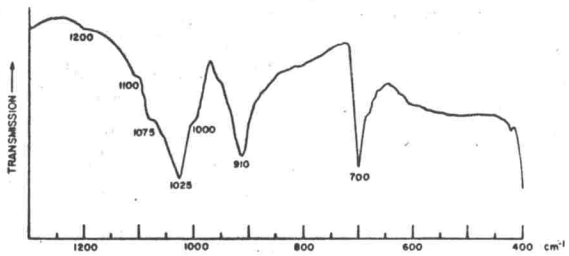

Figure 1. Infrared Spectrum of Mercury Metaborate.

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	WSh	$(\nu_2+\nu_6)$, or $(\nu_1+\nu_6)$
		1075	WSh	
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 α– and β–B_2O_3. The formation of some dense β–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 β–B_2O_3 that B has an average coordination number of 3.4, while in α–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		α—B_2O_3 [a]		β—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:

$$(1)\quad 2HgO + B_2O_3 \xrightarrow[770°C,\,40\,hrs]{30\ Kbar} \underset{product}{yellow} \xrightarrow[250°C,\,5\,hrs]{H_2} \frac{1}{3}[Hg_4O(BO_2)_6] + \frac{2}{3}Hg + \frac{2}{3}H_2O$$

$$(2)\quad 13HgO + 6BN \xrightarrow[940°C,\,10\,hrs]{40\ Kbar} Hg_4O(BO_2)_6 + 9Hg + 3N_2$$

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.