This would account for the over-all stoichiometry, although it cannot be ascertained whether B_2O_3 is produced in a primary reaction or by subsequent decomposition of $H_2B_2O_3$.

The most stable isomer of BH_3O_2, from the point of view of bond strengths, is $HB(OH)_2$. Calculations based on thermochemical data[5,19,20] give for the reactions

$$HB(OH)_2(g) + H_2B(OH)(g) = H_2B_2O_3(g) + 2H_2(g) \qquad (22)$$

and

$$HB(OH)_2(g) + H_2B(OH)(g) = B_2O_3(s) + 3H_2(g) \qquad (23)$$

enthalpy changes of +24 and −81 kcal, respectively. *This indicates that at ordinary temperatures, only* reaction 22 is thermodynamically favorable. Rearrangement of H_2BOOH to $HB(OH)_2$ should then lead to the formation of $B_2O_3(s)$ rather than $H_2B_2O_3(g)$. This type of rearrangement has been observed by Petry and Verhoek.[7a] They observed that the initial product in the gas phase reaction between $B(CH_3)_3$ and O_2, $(CH_3)_2BOOCH_3$, subsequently rearranged to form $(CH_3O)_2BCH_3$.

The mechanism of oxidation of tetraborane is very similar to that described for the $BH_3CO–O_2$ reaction. Boroxine is not produced in this reaction and results of *experiments using oxygen enriched in* $^{18}O_2$ *suggest that* the precursor to $H_2B_2O_3$ is formed initially without rupture of the O–O bond as in the case of the $BH_3CO–O_2$ reaction. Formation of BH_3O_2 is more easily visualized in the reaction of O_2 with B_4H_{10} than in the $B_5H_9–O_2$ reaction. Tetraborane contains two terminal BH_2 groups bridged by hydrogen atoms to the other two boron atoms. Splitting off of two BH_3 groups to form two BH_3O_2 molecules is quite feasible and this would account for the stoichiometry in reaction 7 (*i.e.*, consumption by B_4H_{10} of twice as much O_2 as in the BH_3CO case). Some evidence for this type of fission of tetraborane is given by the formation of $BH_3 \cdot py$ and $B_2H_4 \cdot py$ from tetraborane and pyridine at 0°.[21] The B_2H_4 residue can give rise to diborane and borane polymer as in the case of the $B_5H_9–O_2$ reaction. A similar reaction sequence corresponding to eq 16–18 can easily be written. The stoichiometry observed here of B_4H_{10} with respect to O_2 is the same as that reported by Ludlum,[22] although the over-all reaction stoichiometry is not the same.

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Notes

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The Crystal Structure of a New Polymorph of CrOOH

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Preparation of a new polymorph of chromium oxide hydroxide (CrOOH) by hydrothermal methods was reported by Tombs, Croft, Carter, and Fitzgerald;[1] the compound was identified by chemical analysis and by an X-ray diffraction powder pattern, which was indexed on an orthorhombic cell with a = 4.861 A, b = 4.292 A, and c = 2.960 A. The powder pattern of orthorhombic CrOOH is very similar to that of indium oxide hydroxide (InOOH),[2] the orthorhombic cell is comparable with the unit cell of InOOH, and the two compounds are probably isomorphous. An investigation of the crystal structure of orthorhombic CrOOH was undertaken in order to compare the two crystal structures.

Rhombohedral CrOOH[3,4] has a layer structure. Oxygen atoms are coordinated with chromium atoms in distorted octahedra. Each octahedron is sharing its six edges with six surrounding coplanar octahedra to form continuous sheets in which the oxygen atoms are close-packed. The sheets are superposed so that oxygen atoms of one sheet fall directly above those of the sheet below. The structure as a whole is therefore not close-packed and the layers are held together by short hydrogen bonds.

In structures of compounds with composition MOOH the metal atom is generally octahedrally coordinated with six oxygen atoms. In some rare earth oxide hydroxides a seven-coordination of the metal atom with oxygen atoms has been reported.[5,6] A survey of common MOOH structures has been given by Wells.[7]

A powder sample of orthorhombic CrOOH, kindly put at our disposal by the authors of ref 1, was used in the present investigation. The sample was sealed in a Lindemann glass capillary of 0.25-mm diameter. Intensities of 24 lines of the powder pattern were collected with an automatic single crystal diffractometer using Mo Kα radiation and balanced filters techniques with a scintillation counter. The diffractometer was manually operated and the intensity of each powder

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[1] N. C. Tombs, W. J. Croft, J. R. Carter, and J. F. Fitzgerald, *Inorg. Chem.*, **3**, 1791 (1964).

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[3] R. M. Douglass, *Acta Cryst.*, **10**, 423 (1957).

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[5] A. N. Christensen, *Acta Chem. Scand.*, **19**, 1391 (1965).

[6] R. F. Klevtsova and P. V. Klevtsov, *Zh. Strukt. Khim.*, **5**, 860 (1964).

[7] A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, London, 1962, pp 556–560.

line was obtained as an average of ten measurements. From the strongest lines in the powder pattern 17 independent structure factors were calculated. No absorption correction was applied.

Orthorhombic CrOOH proved to be isostructural with InOOH.[2] The crystal structure of CrOOH is a deformed rutile structure. Oxygen atoms are coordinated with chromium atoms in distorted octahedra. One set of octahedra with chromium at (0, 0, 0) are sharing edges and are stacked along the (0, 0, 1) direction. Another set of octahedra with chromium at ($^1/_2$, $^1/_2$, $^1/_2$) are also sharing edges and are stacked along the (0, 0, 1) direction. The two sets of octahedra are sharing corners and are held together by rather short hydrogen bonds.

An R value ($R = \Sigma||F_o| - k|F_c||/\Sigma|F_o|$) of 11.0% was obtained on inserting Cr and O atoms in the structure factor calculations using the coordinates of In and O in InOOH. Inserting the Cr atoms only gave an R value of 18.7%. Coordinates and temperature factors were refined by the method of Bhuiya and Stanley.[8] The structure factors were calculated using the atomic scattering factors from Vol. III of the International Tables of X-Ray Crystallography and the interpolation formula of Bassi.[9] The refinement yielded an R value of 9.6%.

The crystallographic data obtained are: crystal system, orthorhombic; a = 4.861 A, b = 4.292 A, c = 2.960 A; space group, No. 58, Pnnm; density calculated for two formula units in the unit cell, 4.57 g/cm^3; absorption coefficient μ = 89 cm^{-1} for Mo Kα radiation (λ 0.7107 A).

TABLE I

ATOMIC COORDINATES AND TEMPERATURE FACTORS

Atom	Positions	x	σ_x	y	σ_y	z	B, A^2	σB, A^2
Cr	2(a)	0.0		0.0		0.0	0.4	0.3
O	4(g)	0.361	0.013	0.230	0.020	0.0	8	2

Table I gives atomic coordinates and temperature factors with their standard deviations. Table II gives interatomic distances. The Cr–O distance of 2.0 ± 0.1 A is comparable with the distance of 1.97 ± 0.04 A found in rhombohedral CrOOH.[3] The O–O distance of 2.4 ± 0.2 A corresponds to a hydrogen bond. In InOOH a hydrogen bond of 2.58 A was found. Table III gives X-ray data for orthorhombic CrOOH with observed and calculated intensities.

TABLE II

INTERATOMIC DISTANCES l AND STANDARD DEVIATIONS σ_l IN A

	l	σ_l
Cr–O	2.0	0.07
O–O between octahedra	2.4	0.1
O–O within octahedra	2.8	0.1

TABLE III

X-RAY DIFFRACTION DATA FOR CrOOH

$h\ k\ l$	d_{calcd}, A	I_{obsd}	I_{calcd}	$h\ k\ l$	d_{calcd}, A	I_{obsd}	I_{calcd}
1 1 0	3.217	276	306	0 3 1	1.288	15	15
1 0 1	2.528	74	85	2 0 2	1.264	12	15
0 1 1	2.437	228	172	1 3 1	1.245	2	1
2 0 0	2.430		65	2 3 0	1.233	1	1
1 1 1	2.178	30	20	0 2 2	1.218	15	10
0 2 0	2.146	35	20	4 0 0	1.215		5
2 1 0	2.115	24	14	2 1 2	1.213		1
2 1 1	1.721	103	101	3 2 1	1.185	19	20
1 2 1	1.636	139	117	2 3 1	1.138	19	21
2 2 0	1.609	60	44	2 2 2	1.089	37	18
3 1 0	1.516	31	34	4 1 1	1.088		17
0 0 2	1.480	20	22	0 4 0	1.073	3	5
3 0 1	1.421	43	35	3 1 2	1.059	29	16
1 3 0	1.372	38	48	4 2 0	1.057		9
1 1 2	1.345	31	40				

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Mössbauer Effect in Iron(III) Dithiocarbamates

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According to ligand field theory, the magnetic moments of d^4, d^5, d^6, and d^7 transition metal complexes depend on the relative values of the mean spin-pairing energy π and the strength of the cubic ligand field parameter Δ. Thus, in the case of Fe$^{\text{III}}$ (3d^5 configuration) the magnetic moment is about 5.9 BM in high-spin complexes (weak ligand fields) and 2.9 BM in low-spin or spin-paired complexes (strong ligand fields).[2]

Cambi and co-workers[2–6] have investigated the magnetic properties of some iron(III) tris(dithiocarbamates) [Fe$^{\text{III}}$(DTC)$_3$] and found magnetic moments between 2.3 and 5.9 BM depending on the substituents in the DTC ligands; furthermore, measurements between 84 and 300°K showed that the magnetic moments increased with temperature. More

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