

Yttrium Carbonate Hydroxide

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Abstract. YOHCO_3 , orthorhombic, $P2_12_12_1$; $a = 4.809$ (1), $b = 6.957$ (1), $c = 8.466$ (1) Å; $Z = 4$, $d_c = 3.89$ g cm $^{-3}$. The final R for 737 reflections was 0.0518. The carbonate-group distances and angles are C–O(1) 1.288 (9), C–O(2) 1.279 (9), C–O(3) 1.287 (8) Å, O(1)–C–O(2) 122.8 (7), O(1)–C–O(3) 118.7 (6), and O(2)–C–O(3) 118.3 (7)°. The carbonate ion is bidentate to two different Y atoms. The distortion in the angles of the carbonate is attributed to this bonding scheme. The Y atoms' coordination is a monocapped square antiprism with two hydroxyls and seven carbonate oxygens surrounding the Y.

Introduction. Commercially available yttrium carbonate powder was placed in a 9% solution of NH_4Cl saturated with CO_2 . The solution was then heated in a hydrothermal reactor for 7 d at 360°C and 750 atm. Intensity data were collected on a Syntex $P2_1$ automated diffractometer with Mo $K\alpha$ X-radiation and a graphite monochromator ($\lambda = 0.71069$ Å). A set of 737 unique reflections with $I \geq 3\sigma$ was obtained with $2\theta \leq$

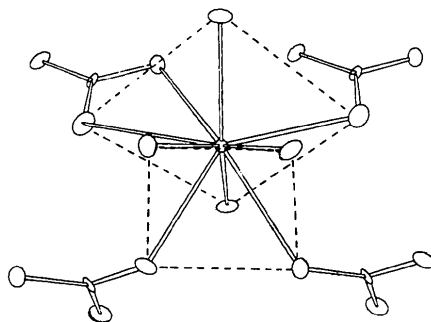


Fig. 1. Drawing of the coordination polyhedron of Y in YOHCO_3 . One of the bidentate carbonates projecting towards the reader has been omitted for clarity.

70°. An absorption correction was applied, the crystal being approximated as a non-reentrant polyhedron with $\mu = 208.5$ cm $^{-1}$. Transmission factors varied from 0.35 to 0.71. The structure was solved with the Patterson function and refined anisotropically with full-matrix least squares to a conventional $R = 0.0518$. Atom coordinates and thermal parameters are listed in Table 1. Interatomic distances less than 3.0 Å and angles in the carbonate ion are listed in Table 2.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31920 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Bond distances (Å) and angles (°)

Symmetry code	(a)	x, y, z	(c)	$\frac{1}{2} + x, \frac{1}{2} - y, -z$
	(b)	$\frac{1}{2} - x, -y, \frac{1}{2} + z$	(d)	$-x, \frac{1}{2} + y, \frac{1}{2} - z$
Y–O(1)	(a)	2.430 (7)	O(1)–O(4)	(d) 2.895 (9)
	(c)	2.430 (7)		(c) 2.976 (9)
	(d)	2.943 (8)		
Y–O(2)	(d)	2.470 (6)	O(1)–O(2)	(b) 2.871 (9)
			(d)	2.771 (10)
	(d)	2.463 (6)	(a)	2.254 (9)
Y–O(3)	(a)	2.478 (6)	O(1)–O(3)	(a) 2.613 (9)
	(d)	2.616 (7)	(c)	2.786 (10)
	(c)	2.615 (6)	(a)	2.216 (9)
Y–O(4)	(d)	2.236 (6)	O(3)–O(4)	(d) 2.698 (8)
	(a)	2.252 (5)	(a)	2.927 (9)
			O(2)–O(3)	(d) 2.863 (9)
		(a)	2.204 (9)	
		(b)	2.982 (8)	
C–O(1)	(a)	1.288 (9)	O(1)–C–O(2)	122.8 (7)
C–O(2)	(a)	1.279 (9)	O(1)–C–O(3)	118.7 (6)
C–O(3)	(a)	1.287 (8)	O(2)–C–O(3)	118.3 (7)

Table 1. Atomic parameters in fractional coordinates and thermal parameters with e.s.d.'s ($\times 10^4$)Temperature factor: $\exp [-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Y	0.0120 (1)	0.1157 (1)	0.1637 (1)	411 (3)	19 (1)	22 (1)	–0.2 (2)	2 (2)	8 (1)
O(1)	0.2884 (12)	0.3951 (11)	0.0935 (8)	101 (19)	43 (9)	37 (6)	–31 (24)	–47 (12)	23 (13)
O(2)	0.4887 (13)	0.5533 (9)	0.2961 (8)	131 (24)	63 (8)	25 (5)	25 (27)	–32 (21)	–37 (11)
O(3)	0.7469 (12)	0.4149 (9)	0.1135 (7)	69 (20)	52 (12)	20 (6)	70 (23)	50 (16)	9 (12)
O(4)	0.0025 (14)	0.7969 (7)	0.1182 (6)	162 (25)	25 (5)	23 (5)	–1 (25)	–46 (19)	–2 (10)
C	0.5043 (13)	0.4514 (8)	0.1707 (7)	44 (21)	29 (8)	16 (5)	–18 (24)	13 (25)	6 (1)

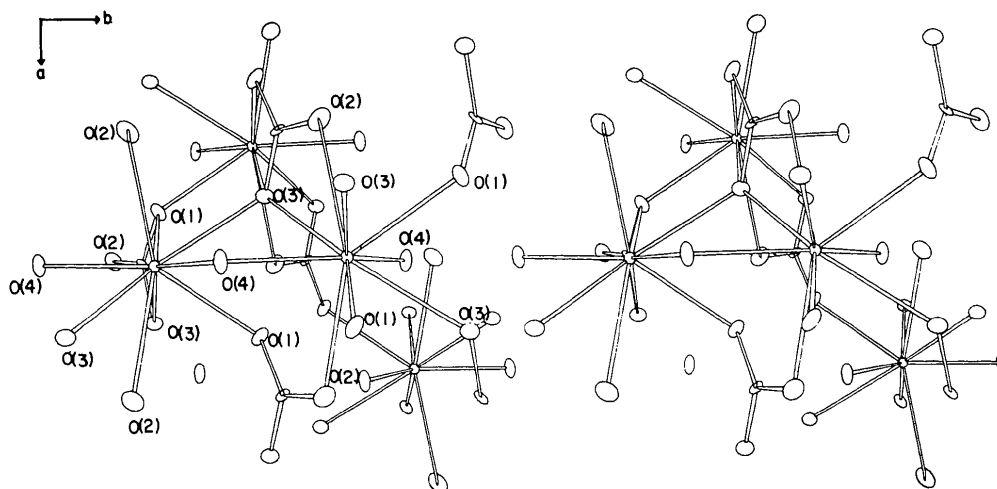


Fig. 2. Stereo view of YOHCO_3 .

Discussion. The structure of NdOHCO_3 has been reported by Christensen (1973). The structure is hexagonal, space group $P\bar{6}$. The Nd is nine-coordinate with a coordination polyhedron shaped like a tricapped trigonal prism. YOHCO_3 is orthorhombic, space group $P2_12_12_1$. The Y is also nine-coordinate (Fig. 1), but its coordination polyhedron is a monocapped square antiprism. This polymorphism may be due to the relative size of Y versus Nd. Two other major differences exist between the structures. First, in the case of Nd the coordination polyhedron contains three hydroxyl groups; the Y only contains two. And secondly, the carbonate ion in the Y structure is bidentate to two different metal atoms; in the Nd structure the carbonate ion is bidentate to only one metal. The C–O distances are in good agreement with the 1.28 Å found in many other carbonate structures. The angles of the carbonate deviate markedly from 120°. This can be explained by the fact that the carbonate ion, which is bidentate to two different metals, causes two of the angles to be 118.3 and 118.7° while the third is 122.8°. The metal-to-oxygen distances can be divided into three groups. The hydroxyl distances are the shortest, 2.236 (6) and 2.252 (5) Å. The metal-to-oxygen distances for the carbonate ion have five bonds approximately 2.45 Å and two longer distances of 2.616 (7) and 2.615 (6) Å. There is a tenth metal-to-oxygen distance of 2.94 (8) Å.

This metal-to-oxygen distance is too long to be considered as part of the Y coordination sphere. The hydroxyl group is 2.895 (9) Å from O(1) and 2.698 (8) Å from O(3), which indicates possible hydrogen bonds. The O(4)–O(1) bond distance is supported by the OH stretching frequency of 3495 cm^{-1} in the Raman spectra. The oxygens of the carbonate ion have two types of coordination. O(1) and O(2) are each coordinated to two Y and one C. O(3) is coordinated to three Y and one C. A drawing of the coordination polyhedron around Y can be seen in Fig. 1. Fig. 2 is a stereo plot of the structure.

A second type of yttrium carbonate crystals has recently been made as described above, except that the temperature in the hydrothermal reactor was 400°C. Preliminary X-ray diffraction studies suggest that these crystals are similar to Christensen's (1973) NdOHCO_3 .

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Reference

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International Union of Crystallography Report of the Executive Committee for 1975

The Report of the Executive Committee for 1975 has been published in *Acta Crystallographica*, Section A [*Acta Cryst.* (1976), A **32**, 1019–1033]. It reports as usual on the meetings

and publications of the Union, the work of its Commissions, and the work of bodies not belonging to the Union but on which the Union is represented.