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Isotope Effects in the Bonds of β-CrOOH and β-CrOOD

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Samples of orthorhombic chromium oxide hydroxide, β-CrOOH, and the deuterated compound, β-CrOOD, were prepared hydrothermally. The crystal structures were determined by powder profile refinement technique using neutron diffraction data. Unit cells are: β-CrOOH: $a = 4.862(2)$ Å, $b = 4.298(2)$ Å, $c = 2.995(1)$ Å; β-CrOOD: $a = 4.873(5)$ Å, $b = 4.332(7)$ Å, $c = 2.963(2)$ Å, with $Z = 2$. The space group is $P2_1nm$ or $Pnnm$. Distances found for the hydrogen atoms using space group $P2_1nm$ are: O–D···O: 2.58(2) Å, O–D: 1.07(2) Å, O–H···O: 2.46(2) Å, and O–H: 1.10(2) Å, showing large isotope effects.

β-Chromium oxide hydroxide, β-CrOOH, and the isomorphous deuterated compound, β-CrOOD, have the indium oxide hydroxide structure (*1–4*). The crystal structure of β-CrOOH was determined using X-ray diffraction powder methods (*3*). A short hydrogen bond of 2.4(1) Å was found, assuming the space group *Pnnm* for the structure (*5*). However, the correct space group for the indium oxide hydroxide structure is $P2_1nm$ (*1*). As the interatomic distances were determined with low precision (*3*), it was decided to reinvestigate the structure of β-CrOOH, using neutron diffraction powder methods. In addition, the structure of the deuterated compound, β-CrOOD, was studied using the same technique. This was done to obtain better counting statistics of the powder pattern due to the low incoherent scattering of a deuterated sample and to study possible cooperative effects in the interatomic distances in going from β-CrOOH to β-CrOOD. In comparisons of interatomic distances in a hydrogen bond of a compound and of the deuterated analog, it is normally found that the distance O–D···O is longer than the distance O–H···O, that O–D is shorter than O–H, and that consequently D···O is longer than H···O. There is thus a cooperative effect. In a previous investigation of the crystal structure of rhombohedral chromium oxide hydroxide, α-CrOOH, and of the corresponding deuterated compound, α-CrOOD, it was assumed that the substitution of D for H did not effect the Cr–O distances, and in consequence of this the structure of chromium oxide hydroxide was refined with the Cr–O distances constrained to the value 1.979(5) Å, using combined α-CrOOH and α-CrOOD data (*6*). However, if the observations found for the hydrogen bonds O–H···O and O–D···O are general, it should also apply

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for the distances D–O–Cr and H–O–Cr, that the distance Cr–O(D) should be longer than the distance Cr–O(H).

Experimental

Chemistry and X-Ray Technique

β-CrOOH was prepared from CrO_2 by reduction with $(COOH)_2 \cdot 2H_2O$ under hydrothermal conditions (*4*). In a typical experiment, 15 g of CrO_2, 36 g of $(COOH)_2 \cdot 2H_2O$ and 178 ml of H_2O were placed in a 260-ml pressure vessel lined with pure gold and kept at 290°C and 100 MPa for 210 hr. The product was washed with water and dried in air. β-CrOOD was prepared hydrothermally from CrO_2 and a solution of $(COOD)_2$ in D_2O. The solution of deuterated oxalic acid was prepared in the following way: 37 g of $(COOH)_2 \cdot 2H_2O$ was kept at 120°C for 5 hr and was then dissolved in 200 ml of D_2O. The solution was evaporated to dryness and the solid was dissolved in 178 ml of D_2O. This solution was placed with 15 g CrO_2 in the pressure vessel and kept at 295°C and 80 MPa for 210 hr. The product was washed with D_2O and dried in air.

X-ray powder patterns were taken of all hydrothermal products using a Guinier camera with Co$K\alpha_1$ radiation ($\lambda = 1.78892$ Å) and sodium chloride ($a_{NaCl} = 5.6389$ Å) as internal standard. The unit cell parameters obtained from these measurements are:

β-CrOOH: $a = 4.862(2)$ Å,
$b = 4.298(2)$ Å,
$c = 2.955(1)$ Å,

β-CrOOD: $a = 4.873(5)$ Å,
$b = 4.332(7)$ Å,
$c = 2.963(2)$ Å.

Neutron diffraction powder patterns of both compounds were obtained using a double-axis neutron spectrometer at the DR3 reactor at Risø. The diffraction patterns were obtained with an incident neutron wavelength $\lambda = 1.6885$ Å. The powder samples (approximately 30 g each) were housed in a thin-walled cylindrical vanadium container. The powder pattern of β-CrOOH was measured in the 2θ interval, 15 to 109°, in steps of 0.1° and that of β-CrOOD was measured in the 2θ interval, 15 to 97°, in steps of 0.1°.

Structure Refinement

The structures of both compounds were refined in the space groups $P2_1nm$ and $Pnnm$, using the Rietveld refinement program for powder profile intensities (*7*, *8*). The scattering lengths (in 10^{-12} cm) were: $b_{Cr} = 0.353$, $b_O = 0.580$, $b_H = -0.374$, and $b_D = 0.667$ (*9*).

TABLE Ia

RESULTS OF THE REFINEMENT OF THE STRUCTURE OF β-CrOOD[a]

Atom	x	y	z	B (Å^2)
Cr	0	0.2384(35)	0	0.68(9)
O1	0.3205(56)	0.4816(25)	0	0.68(9)
O2	0.6207(50)	−0.0075(23)	0	0.68(9)
D	0.5093(52)	0.2044(24)	0	0.68(9)

[a] Scale factor = 0.0201. $R = 5.5\%$. $R(F^2) = 6.0\%$. (For definition of R (profile) and $R(F^2)$ (nuclear), see (*8*).) Total number of refined parameters = 15.

TABLE Ib

OBSERVED AND CALCULATED INTENSITIES OF β-CrOOD

$h\,k\,l$	I_{obs}	I_{calc}	$h\,k\,l$	I_{obs}	I_{calc}
1 1 0	1005	990	3 0 1	2161	1990
1 0 1	6533	6646	2 2 1	938	1134
0 1 1	7118	6770	0 1 2	4	104
2 0 0	1668	1599	1 3 0	35	161
1 1 1	10065	9971	3 1 1	819	951
0 2 0	148	134	1 1 2	271	364
2 1 0	7267	7068	3 2 0	576	439
1 2 0	0	232	0 3 1	766	833
0 2 1	107	158	2 0 2	833	927
2 1 1	5522	5730	1 3 1	2887	2870
1 2 1	1924	1315	2 3 0	1706	1636
2 2 0	4386	4330	0 2 2	96	93
3 1 0	56	161	4 0 0	616	608
0 0 2	5819	5750	2 1 2	5018	5047
0 3 0	587	350	3 2 1	5382	4988

TABLE IIa

RESULTS OF THE REFINEMENT OF THE STRUCTURE OF β-CrOOH[a]

Atom	x	y	z	B (Å^2)
Cr	0	0.2617(41)	0	0.82(8)
O1	0.3788(29)	0.4814(32)	0	0.82(8)
O2	0.6708(31)	0.0142(33)	0	0.82(8)
H	0.5275(64)	0.2110(37)	0	0.82(8)

[a] Scale factor = 0.0050. $R = 4.9\%$. $R(F^2) = 5.6\%$. (For definition of R (profile) and $R(F^2)$ (nuclear), see (*8*).) Total number of refined parameters = 15.

TABLE IIb

OBSERVED AND CALCULATED INTENSITIES FOR β-CrOOH

h k l	I_{obs}	I_{calc}	*h k l*	I_{obs}	I_{calc}
1 1 0	18316	18600	0 1 2	109	116
0 1 1	328	266	1 3 0	5138	6030
2 0 0	1991	1686	3 1 1	2489	2747
1 1 1	34029	33525	1 1 2	5845	6610
0 2 0	12444	12455	1 3 1	11375	11517
2 1 0	25221	24299	2 3 0	8485	8280
1 2 0	829	1030	0 2 2	8646	8393
1 2 1	45551	43179	4 0 0	4285	4113
2 2 0	1666	1289	2 1 2	18632	16745
3 1 0	5541	6172	4 1 1	765	943
0 0 2	7029	6221	0 4 0	3896	3496
0 3 0	884	833	3 3 0	674	606
3 0 1	28537	27571	3 1 2	6863	6785
2 2 1	1522	1510	4 2 0	5318	5295

Refinement in Space Group $P2_1nm$

β-CrOOD. The structure of β-CrOOD was refined using the coordinates from the structure of InOOH as starting parameters (*1*). The parameters refined are seven positional parameters, one overall isotropic temperature factor, and a scale factor. In addition, two half-width parameters, a zero-point parameter, and three unit-cell parameters were refined. Instrumental errors are accounted for by some of these parameters. The results of the refinement are listed in Table I.

As it was a question of whether the hydrogen atom forms a hydrogen bond with the hydrogen atom placed in sites symmetric with respect to the midpoint of the O···O bond, this hypothesis was tried. However, the refinements did not lead to chemically acceptable values for the two half-hydrogen atom positions.

β-CrOOH. The structure of β-CrOOH was refined using the same starting parameters and the same number of parameters as for β-CrOOD. The results of the refinements are listed in Table II. Similar to the case of β-CrOOD, the hypothesis of a symmetric hydrogen bond was tried, but as for β-CrOOD, the results were not chemically meaningful.

Refinement in Space Group Pnnm

β-CrOOD and β-CrOOH. This space group was originally assumed for the structure of InOOH (*5*) and that of β-CrOOH (*3*). The coordinates from the structure of InOOH (*5*) were used as starting parameters. The struc-

TABLE IIIa

RESULTS OF THE REFINEMENT OF THE STRUCTURE OF β-CrOOD IN SPACE GROUP *Pnnm*[a]

Atom	x	y	z	B (Å^2)
Cr	0	0	0	0.15(8)
O1	0.3499(6)	0.2421(9)	0	0.15(8)
D	0.4562(16)	0.0401(26)	0	0.15(8)

[a] Scale factor = 0.0207. $R = 6.4\%$. $R(F^2) = 8.0\%$. Total number of refined parameters = 12.

TABLE IIIb

RESULTS OF THE REFINEMENT OF THE STRUCTURE OF β-CrOOH IN SPACE GROUP *Pnnm*[a]

Atom	x	y	z	B (Å^2)
Cr	0	0	0	0.62(8)
O1	0.3527(9)	0.2357(10)	0	0.62(8)
H	0.4994(49)	0.0395(41)	0	0.62(8)

[a] Scale factor = 0.0051. $R = 5.1\%$. $R(F^2) = 5.6\%$. Total number of refined parameters = 12.

TABLE IVa

INTERATOMIC DISTANCES IN Å WITH STANDARD DEVIATIONS IN PARENTHESES: SPACE GROUP $P2_1nm$

β-CrOOD		Average	β-CrOOH		Average
O2–O1	2.58(2)		O2–O1	2.46(2)	
O2–D	1.07(2)		O2–H	1.10(2)	
D–O1	1.51(2)		H–O1	1.37(2)	
Cr–O1	1.88(2)	1.99(2)	Cr–O1	2.07(2)	2.01(2)
Cr–O1′	2.11(2)		Cr–O1′	1.94(2)	
Cr′–O2	2.13(2)	2.01(2)	Cr′–O2	1.92(2)	1.99(2)
Cr–O2′	1.88(2)		Cr–O2′	2.07(2)	

Note: Cr′ is at $1 + x, y, z$; O1′ is at $x - 0.5, 1 - y, z + 0.5$; O2′ is at $x - 0.5, -y, z + 0.5$.

TABLE IVb

INTERATOMIC DISTANCES IN Å WITH STANDARD DEVIATIONS IN PARENTHESES: SPACE GROUP $Pnnm$

β-CrOOD		Average	β-CrOOH		Average
O2–O1	2.56(1)		O2–O1	2.48(1)	
O2–D	1.02(1)		O2–H	1.10(1)	
D–O1	1.55(1)		H–O1	1.38(1)	
Cr–O1	1.99(1)	1.99(1)	Cr–O1	1.99(1)	2.00(1)
Cr–O1′	1.99(1)		Cr–O1′	2.00(1)	

Note: O1′ is at $x - 0.5, 0.5 - y, z + 0.5$; O2 is at $1 - x, -y, z$.

ture has a hydrogen bond where a half-hydrogen atom is placed in site 4g. From packing considerations, the value for the coordinate of this half-hydrogen (deuterium) atom was assumed to be (0.50, 0.07, 0). Four positional parameters, one scale factor, and one overall isotropic temperature factor were refined. In addition, two half-width parameters, a zero-point parameter, and three unit-cell parameters were refined. The results of the refinements are listed in Table IIIa. In the same way the structure of β-CrOOH was refined, and the results obtained are listed in Table IIIb.

Interatomic distances calculated from the coordinates (Tables I, II, and III) and the unit-cell parameters obtained from the Guinier powder patterns are listed in Table IV. Figure 1 shows the packing of atoms in the

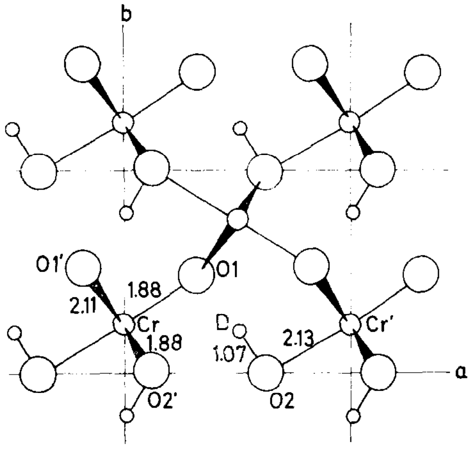

FIG. 1. Projection of the structure of β-CrOOD along (001) in space group $P2_1nm$. Standard deviations on all distances are 0.02 Å.

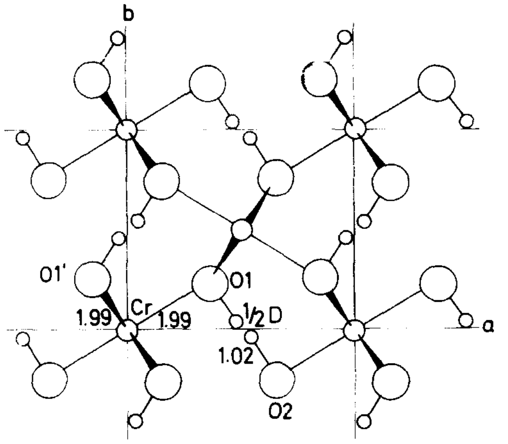

FIG. 2. Projection of the structure of β-CrOOD along (001) in space group *Pnnm*. Standard deviations on all distances are 0.02 Å.

structure of β-CrOOD assuming the space group $P2_1nm$, and Fig. 2 shows the structure of β-CrOOD assuming the space group *Pnnm*.

Discussion

With the profile refinement method used, it is apparently not possible to distinguish between the structural model of β-CrOOH and β-CrOOD for the two space groups investigated. The atomic coordinates obtained for the two models are significantly different from each other (see Tables I, II, and III). The interatomic distances are, however, not significantly different from each other for the two models (see Tables IVa and IVb). (The coordinates for the atoms in β-CrOOH found in the refinements using space group $P2_1nm$ are similar to the atomic coordinates of the high-pressure modification of iron oxide hydroxide, FeOOH, refined in the same space group (*10*).) From the interatomic distances in Table IVa it can be seen that the short hydrogen bonds in β-CrOOD and β-CrOOH are not centered, and that the cooperative effect is observed for the hydrogen bonds. The O–D···O distance of 2.58(2) Å is significantly longer than the O–H···O distance of 2.46(2) Å, the O–H distance of 1.10(2) Å is longer than the O–D distance of 1.07(2) Å, and the D···O distance of 1.51(2) Å is significantly longer than the H···O distance of 1.37(2) Å. The refinements of the two structures in the space group *Pnnm* also show that the short hydrogen bonds are not centered (see Table IVb).

The Cr–O distances found in the two compounds have average values of 2.00(2) Å. In the space group $P2_1nm$ the atom O1 is an O^{2-} ion and the atom O2 belongs to an OD^- or OH^- ion (see Fig. 1). The average values of the Cr–O distances for the two types of ions are not significantly different from each other for the two compounds (see Tables IVa and IVb). At this level of precision, the assumption of identical Cr–O distances in the two compounds is obviously justified. The average distance Cr–O2 in β-CrOOD of 2.01(2) Å is longer than the average distance Cr–O2 in β-CrOOH, 1.99(2) Å, but the difference between these two values is so small that no conclusion can be drawn concerning a cooperative effect in the bonds D–O–Cr and H–O–Cr.

The structures of the two compounds investigated contain CrO_6 octahedra stacked in the (001) direction on octahedra edges. These columns of octahedra share oxygen atoms and are, in addition, held together by the short hydrogen bonds (see Fig. 1). Figure 3 shows a projection of the structure of β-CrOOH along the (001) direction. In the structure of β-CrOOH the Cr–O2' distances is long, 2.07(2) Å, and the Cr'–O2 distances are

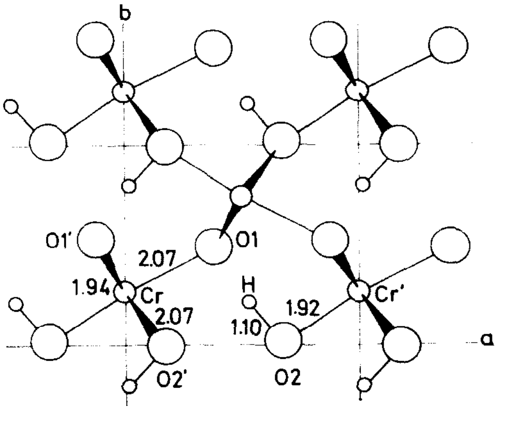

FIG. 3. Projection of the structure of β-CrOOH along (001) in space group $P2_1nm$. Standard deviations on all distances are 0.02 Å.

short, 1.92(2) Å. In the structure of β-CrOOD the Cr–O2′ distances are short, 1.88(2) Å, and the Cr′–O2 distances are long, 2.13(2) Å. The chromium atom is not centered in the CrO_6 octahedra and can be placed in different positions, as can be seen in the Figs. 1 and 3, and from the chromium atom coordinates in Tables Ia and IIa.

This apparent discrepancy for the chromium atom coordinates can be greatly reduced by a change in origin for the β-CrOOD structure (inversion through the origin followed by a shift of the origin to 0, $\frac{1}{2}$, 0). The coordinates for the chromium and oxygen atoms in β-CrOOD would then be very similar to the values listed for β-CrOOH in Table IIa. The position of the deuterium atom would then be on the other side of the hydrogen bond.

The refinement of the different models of the structures of β-CrOOH and β-CrOOD shows that the data were insufficient to permit unambiguous choice between the models. This investigation shows, however, without ambiguity, that the hydrogen bonds in the two compounds are not centered.

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