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

A. NØRLUND CHRISTENSEN

Department of Inorganic Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

P. HANSEN

Department of Physics, Risø, DK-4000 Roskilde, Denmark

AND

M. S. LEHMANN

Institut Max von Laue—Paul Langevin, B.P. 156, F-38042 Grenoble Cedex, France

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Samples of rhombohedral chromium oxide hydroxide, α-CrOOH, and the deuterated compound, α-CrOOD, were prepared hydrothermally. The crystal structures were determined by powder profile refinement technique using neutron diffraction data. The crystallographic data are: α-CrOOH: $a = 2.979(5)$ Å, $c = 13.37(2)$ Å, $z = 3$, space group $R\bar{3}m$ (No. 166). α-CrOOD: $a = 2.985(4)$ Å, $c = 13.48(3)$ Å, $z = 3$, space group $R3m$ (No. 160). Distances found for the hydrogen (deuterium) atoms are: O–D ··· O: 2.57(2) Å; O–D: 1.05(2) Å; O–H ··· O: 2.47(1) Å; and O–H: 1.16(1) Å, showing large isotope effects.

Alpha chromium oxide hydroxide, α-CrOOH, and the isomorphous deuterated compound, α-CrOOD, have a layer crystal structure, where close-packed CrO_6-octahedra are held together by short hydrogen bonds. Only a few metal oxide hydroxides have that type of structure. The crystal structure was determined by Douglass (*1*) from an X-ray diffraction powder pattern and refined using the centrosymmetric space group $R\bar{3}m$. Using neutron diffraction powder patterns of α-CrOOH and α-CrOOD, Hamilton and Ibers (*2*) investigated the hydrogen bondings in the two compounds. They found that the space group was centrosymmetric, and that the bond O–D–O was a noncentered hydrogen bond with an O–O distance of 2.48(3) Å and an O–D distance of 1.02(4) Å. This involves a random distribution of the deuterium atoms in the site 6*c* with $z = 0.4834(35)$ (hexagonal setting is used throughout the paper) with $\frac{1}{2}$D placed on each side of a center of symmetry. For the compound α-CrOOH Hamilton and Ibers (*2*) could not determine if the hydrogen atom was placed in site 3*b* with $z = 0.5$, which is a centered hydrogen bond, or if it was arranged at random in site 6*c*, yielding an acentered hydrogen bond as described above for α-CrOOD. The distribution of H in the bond O–H–O in α-CrOOH was thus undetermined. Rush and Ferraro (*3*) made an investigation of the hydrogen bonding in α-CrOOH using spectroscopic methods. A comparison of the neutron and infrared results appears to raise some uncertainty concerning the assumption of centered hydrogen bonds in α-CrOOH. As the hydrogen bond in α-CrOOH is short and as it is of interest to know if short hydrogen bonds are centered, it was decided to make a reinvestigation of the crystal structure of α-CrOOD and α-CrOOH using elastic neutron scattering.

Experimental

A powder sample of α-CrOOH was made by hydrolysis of an aqueous solution of sodium chromate under hydrothermal conditions (*4*). Samples of α-CrOOD were made in a similar

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way with water in all solutions substituted by D_2O. The unit cell parameters were calculated from Guinier powder photographs obtained with a Guinier de Wolff camera using $CoK\alpha_1$ radiation, $\lambda = 1.78892$ Å, and germanium, $a_{Ge} = 5.6576$ Å, as an internal standard. The unit cell parameters obtained from these measurements are:

α-CrOOH: $a = 2.979(5)$ Å
$c = 13.37(2)$ Å
α-CrOOD: $a = 2.985(4)$ Å
$c = 13.48(3)$ Å.

α-CrOOD. A neutron diffraction powder pattern of α-CrOOD was measured at Risø using neutrons of a wave length $\lambda = 1.665$ Å. The diagram was measured in the 2θ interval 10 to 95° in steps of 0.1°. The diagram showed nine resolved peaks corresponding to contributions from 14 reflections. In addition the diagram had four peaks from an impurity of Cr_2O_3. These peaks did not overlap with any of the peaks belonging to α-CrOOD.

α-CrOOH, data I. A neutron diffraction powder pattern of α-CrOOH was measured at Risø at 300°K using neutrons of wavelength $\lambda = 2.380$ Å. A two-axis spectrometer installed at the cold neutron source was used for this experiment. The high-neutron flux from the cold source gives better counting statistics than for diagrams measured with the spectrometer used for α-CrOOD. The relative long wavelength gives a diagram with only eight peaks corresponding to contributions from nine reflections. The diagram was measured in the 2θ interval 20–110° in steps of 0.1°.

α-CrOOH, data II. Another neutron diffraction powder pattern of α-CrOOH was measured at 4.2°K at the D1A spectrometer in the Laue–Langevin Institute in Grenoble, using neutrons of wavelength $\lambda = 1.389$ Å. The diagram was measured in the 2θ interval 3.0 to 154.5° in steps of 0.05°. The diagram had 32 resolved peaks with contributions from 45 reflections.

Structure Refinement

The structures of both compounds were refined in the space groups $R3m$ and $R\bar{3}m$, using the Rietveld refinement program for powder intensities (*5*, *6*). The scattering lengths (in 10^{-12} cm) were: $b_{Cr} = 0.353$, $b_O = 0.580$, $b_H = -0.374$, and $b_D = 0.667$ (*7*).

α-CrOOD. (a) Space group $R\bar{3}m$. The positional parameters reported by Hamilton and Ibers for the oxygen atom and for the deuterium atom were used as starting parameter. The parameters used in the refinement are two positional parameters, one overall temperature factor, and a scale factor. The refinement converged very slowly (more than 20 cycles) to the positional parameters listed in Table I. This corresponds to a hydrogen bond distance O–D–O: 2.56(2) Å and an oxygen deuterium distance of 1.02(2) Å.

TABLE Ia

RESULTS OF THE REFINEMENT OF THE STRUCTURE OF α-CrOOD

Space group	$R\bar{3}m$	$R3m$
Atom site	6*c*	3*a*
Atomic parameter	*z*	*z*
Cr	0	0
O1	0.4049(12)	0.4091(44)
O2		0.6000(45)
D	0.4803(13)	0.4868(36)
Scale factor	0.0088(3)	0.0086(3)
Temperature factor B (Å^2)	0.25(18)	0.54(20)
R^a	13.3%	7.6%
$R(F^2)$	16.9%	9.1%
Number of parameters	4	5

[a] R is the profile agreement factor. For a definition of R and $R(F^2)$ see (*6*).

TABLE Ib

OBSERVED AND CALCULATED INTENSITIES OF α-CrOOD, $R3m$

h k l	I_{obs}	I_{calc}	*h k l*	I_{obs}	I_{calc}
0 0 3	217	208	1 1 0	9699	9864
1 0 1	9357	9118	0 2 1	2439	2605
0 1 2	11 118	10 540	2 0 2	3351	3255
0 0 6	1028	370	1 1 6	408	382
0 1 5	4063	2994	0 2 4	248	170
1 0 7	886	777	1 0 10	5252	5141
0 0 9	442	552	2 0 5	1746	1341

(b) Space group $R3m$. The starting parameters for the two oxygen atoms and for the deuterium atom were derived from the positional parameters from the refinement in space group $R\bar{3}m$. Three positional parameters, a scale factor, and an overall temperature factor are used in the refinement. The refinement converged slowly to a model with the positional parameters listed in Table I. This model has a hydrogen bond distance O–D–O: 2.57(2) Å and an oxygen deuterium distance of 1.05(2) Å.

The O–D–O and the O–D distances found for the structure described in space group $R\bar{3}m$ and $R3m$ are not significantly different from each other and are not significantly different from the corresponding distances found by Hamilton and Ibers, (O–D–O: 2.48(3) Å, O–D: 1.02(4) Å). The investigation thus confirms that the bond O–D–O is not a centered hydrogen bond. The best agreement between observed and calculated profile intensities is obtained when the space group $R3m$ is used.

α-CrOOH data I. (a) Space group $R\bar{3}m$. Positional parameters corresponding to a centered hydrogen bond, $z_H = 0.5$, $z_O = 0.4045$, were used as starting values in the refinement. The number of parameters refined is the same as for α-CrOOD. In one cycle the positional parameters shifted to $z_H = 0.4813$, $z_O = 0.4046$, and the refinement then converged very slowly (more than 20 cycles), all with shifts smaller than the standard deviations to the positional parameters listed in Table II.

TABLE II

RESULTS OF THE REFINEMENT OF THE STRUCTURE OF α-CrOOH, DATA I

Space group	$R\bar{3}m$	$R3m$
Atom site	6c	3a
Atomic parameter	z	z
Cr	0	0
O1	0.4079(4)	0.4246(19)
O2		0.6075(17)
H	0.4757(14)	0.4903(22)
Scale factor	0.0019(1)	0.0019(1)
Temperature factor B (Å^2)	0.26(18)	0.31(16)
R	3.1%	1.5%
$R(F^2)$	3.6%	1.7%
Number of parameters	4	5

This model corresponds to a O–H–O distance of 2.46(2) Å, and an O–H distance of 0.91(2) Å. This last distance is rather short. The O–H distance calculated from the coordinates after the first cycle of refinement is 1.03(2) Å.

(b) Space group $R3m$. The value of the parameters $z_{O1} = 0.4079$, $z_{O2} = 0.5921$, $z_H = 0.4864$, were used as initial values in the refinement. The number of parameters varied is the same as for α-CrOOD. The refinement converged slowly (over 13 cycles) to a model with the positional parameters listed in Table II. This model has an O–H–O distance of 2.44(3) Å, and an O–H distance of 0.88(3) Å. These interatomic distances do not deviate significantly from the distances for the model described in space group $R\bar{3}m$.

The calculations using the two space groups and data I show unambiguously that the O–H–O bond is not centered. This set of data is, however, insufficient to give physically meaningful values for the O–H distance in the OH^--ion.

α-CrOOH data II. (a) Space group $R3m$. The atomic positional parameters obtained in the refinement with data I were used as starting parameters. The parameters varied are three positional parameters, an overall temperature factor, a scale factor, three half-width parameters, a zero point parameter, two unit cell parameters, a preferred orientation parameter, and an asymmetry parameter, giving a total of 13 parameters. Refinements using individual isotropic temperature factors for the atoms resulted in negative values for the temperature factor of O1. The refinement gave a model with the positional parameters listed in Table III. This model gives an O–H–O distance of 2.47(1) Å, and O–H distances of 1.07(1), and 1.40(1) Å, respectively. It is assumed that these distances are comparable to the distances at room temperature as the contraction in bonds is usually smaller than the standard deviations obtained in this investigation.

(b) Space group $R\bar{3}m$. The atomic positional parameters obtained in the refinement of data I and the profile parameters obtained in the refinement described above were used as starting parameters. Two positional parameters, three isotropic temperature factor parameters, and the same number of profile

TABLE IIIa

RESULTS OF THE REFINEMENT OF THE STRUCTURE OF α-CrOOH, DATA II

Space group	$R3m$	$R\bar{3}m$	
Atom site	3*a*	6*c*	
Atomic parameter	*z*	*z*	B (Å²)
Cr	0	0	0.50(5)
O1	0.4080(11)	0.4076(1)	0.48(3)
O2	0.5926(11)		
H	0.5128(11)	0.4940(14)	1.68(9)
Scale factor	0.1910	0.1902	
Temperature factor B (Å²)	0.60(3)		
R	10.4%	8.1%	
$R(F^2)$	11.4%	8.8%	
Number of parameters	13	14	

TABLE IIIb

OBSERVED AND CALCULATED INTENSITIES OF α-CrOOH, R$\bar{3}m$, DATA II

h k l	I_{obs}	I_{calc}	*h k l*	I_{obs}	I_{calc}
0 0 3	3864	3101	1 0 13	53	32
1 0 1	207	291	2 1 4	712	636
0 1 2	810	788	0 2 10	867	750
0 0 6	1231	1090	1 2 5	4021	3717
1 0 4	1528	1546	0 1 14	143	17
0 1 5	6969	6776	1 1 12	1294	1136
1 0 7	2726	2605	0 0 15	405	361
1 1 0	2108	2213	2 0 11	275	178
0 0 9	18	4	2 1 7	2164	1909
1 1 3	1928	1971	3 0 0	1163	1008
0 1 8	2	1	3 0 3	861	742
0 2 1	24	109	1 2 8	13	1
2 0 2	273	280	0 2 13	60	21
1 1 6	2107	2093	0 3 6	1165	1064
0 2 4	572	524	1 0 16	609	490
1 0 10	1049	1012	2 1 10	1458	1467
2 0 5	2797	2773	2 0 14	91	13
0 0 12	265	239	1 1 15	2150	2114
0 1 11	188	209	1 2 11	615	406
0 2 7	1337	1315	2 2 0	1284	1162
1 1 9	14	4	0 0 18	34	34
2 1 1	126	173	2 2 3	896	815
1 2 2	413	412			

parameters as were used above, giving a total of 14 refined parameters. The positional parameters of this model are listed in Table III. The hydrogen bond O–H–O in this model is 2.47(1) Å and the O–H distances are 1.16(1) and 1.31(1) Å, respectively. A refinement with the hydrogen atom fixed at $z_H = 0.5$, the center of the O–H–O bond gave an R-value of 12.5% higher than the value for the noncentered position.

Discussion

For the α-CrOOD data the best agreement between observed and calculated intensities is obtained for a model of the structure refined in space group $R3m$. Figure 1 shows the diagonal plane of the unit cell. The refinement shows without ambiguity that the hydrogen bond O–D···O is not centered. The interatomic distances calculated for the two models (space group $R3m$ and $R\bar{3}m$) are not significantly different from each other, and the O–O distance, 2.57(2) Å, of the hydrogen bond is in good agreement with the value 2.55(2) Å, reported in (*3*).

For α-CrOOH, data I were insufficient to give a model with physical meaningful interatomic distances. For data II the best agreement between observed and calculated intensities is found for the structure refined in space group R$\bar{3}m$. Figure 2 shows the diagonal plane of the unit cell. The refinement shows that the hydrogen atom is not placed in the center of the

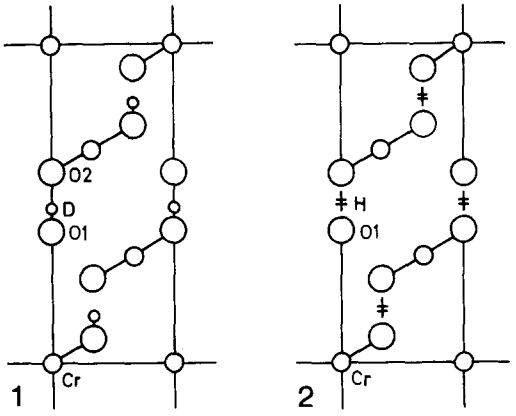

FIG. 1. Diagonal plane of the unit cell for α-CrOOD. Space group $R3m$.

FIG. 2. Diagonal plane of the unit cell for α-CrOOH. Space group $R\bar{3}m$. The positions of the two ½H atoms are indicated by a double cross.

TABLE IV

HYDROGEN BOND DISTANCES

	α-CrOOH	α-CrOOD
O–O	2.47(1)	2.57(2)
O–H(D)	1.16(1)	1.05(2)
H(D)–O	1.31(1)	1.52(2)
	β-CrOOH (*8*)	β-CrOOD (*8*)
O–O	2.46(2)	2.58(2)
O–H(D)	1.10(2)	1.07(2)
H(D)–O	1.37(2)	1.51(2)

bond O–H–O, but is arranged with two $\frac{1}{2}$H atoms on each side of the center of symmetry of the bond. This gives the two O–H distances in the bond, 1.16(1) Å and 1.31(1) Å, that are significantly different from each other. The two "half-hydrogen" atoms are about 0.15(1) Å apart and are placed in an energy potential with a double minimum. They randomly occupy alternative sites slightly to either side of the midpoint of the hydrogen bond. The O–O distance of 2.47(1) Å of the hydrogen bond is in good agreement with the value 2.49(2) Å obtained from spectroscopic data (*3*).

In a comparison between the distances in the hydrogen bonds of α-CrOOD and α-CrOOH (see Table IV), it is found as expected that the O–O distance in α-CrOOD is longer than the O–O distance in α-CrOOH, that the O–D distance is shorter than the O–H distance, and that the O···D distance is longer than the O···H distance. The distances in the hydrogen bonds are also in good agreement with the distances found in the hydrogen bonds of β-CrOOD and β-CrOOH (*8*).

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