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Structures of $HCrO_2$ and $DCrO_2$*

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A neutron diffraction study of polycrystalline $HCrO_2$ and $DCrO_2$ (chromous acid) is described. Intensity data from the two substances were refined together by the least-squares method, with the constraint that the Cr–O distance be the same in the two substances. Estimates of individual contributions to multiple peaks were included in the least-squares refinement through the use of a non-diagonal weight matrix. The O–D–O bond is found to be asymmetric, O–D $= 0{\cdot}96 \pm 0{\cdot}04$ Å, O $\cdots$ O $= 2{\cdot}55 \pm 0{\cdot}02$ Å. The symmetry of the O–H–O bond cannot be determined, but agreement with observation is as good with a symmetric bond as with any other model. The O–H–O bond length is $2{\cdot}49 \pm 0{\cdot}02$ Å. These results are consistent with those from previous studies of the $HCrO_2$–$DCrO_2$ system by nuclear magnetic resonance and infrared techniques.

Introduction

The nature of the hydrogen bonds in $HCrO_2$ and $DCrO_2$ has been the subject of a nuclear magnetic resonance (Ibers, Holm & Adams, 1961) and an infrared investigation (Snyder & Ibers, 1962). It was found in the nuclear magnetic resonance study that, regardless of the actual symmetry of the O–H–O bond, the vibrational amplitude of the hydrogen atom normal to the bond is larger than the amplitude along the bond, a result that is believed to support a symmetric hydrogen bond. The striking differences between the infrared spectra of $HCrO_2$ and $DCrO_2$ are readily explained (Snyder & Ibers, 1962) on the basis of different potential functions for the O–H–O and O–D–O bonds. The lowest vibrational level in the O–H–O system is above a barrier, if any, and the bond is symmetric; the lowest vibrational levels in the O–D–O system are below the barrier, detectable splitting of the energy levels occurs, and the bond is asymmetric†. This appears to be the first pronounced isotope effect in strong hydrogen bonds, although the hypothesis of different potential functions for the H and D systems (Snyder & Ibers, 1962) is thought by Blinc (1962) to explain anomalies in the ratios of ferroelectric transition temperatures in certain systems.

In both the nuclear magnetic resonance and the infrared studies the present neutron diffraction results were alluded to; these results, in abbreviated form, were presented recently (Hamilton & Ibers, 1962). The purposes of this paper are to provide the details of the neutron diffraction study of polycrystalline $HCrO_2$ and $DCrO_2$ and to give an analysis of the data that we now find more satisfying than that given earlier. Nevertheless the conclusions of the earlier analysis hold: the O–D–O bond is asymmetric, but the symmetry of the O–H–O bond remains unresolved in this neutron diffraction study.

Review of the structure of chromous acid

Douglass (1957) in an X-ray study found $HCrO_2$ to be trigonal, $a = 4{\cdot}787$ Å, $\alpha = 36{\cdot}3°$, Laue symmetry $\bar{3}m$, one molecule per unit cell. Douglass placed Cr at (0, 0, 0) and O at $\pm(x_O, y_O, z_O)$ with $x_O = 0{\cdot}405 \pm 0{\cdot}003$ in space group $R\bar{3}m$. Neutron structure factor calculations for a variety of models, including some in which the oxygen atoms are non-equivalent, confirm this structure and indicate that the hydrogen atoms must be placed either randomly with $\frac{1}{2}$H at $\pm(x_H, x_H, x_H)$ or in a symmetric O–H–O bond with H at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The structure (Fig. 1) consists of sheets of Cr atoms between two sheets of O atoms. The O atoms in these sheets are close packed, and each Cr atom is surrounded by a flattened octahedron of O atoms. The O–Cr–O layers are stacked normal to the [111] axis with a three-layer repeat. The separate layers are joined together by hydrogen bonds.

Previously the neutron diffraction data (Hamilton & Ibers, 1962) from polycrystalline samples of $HCrO_2$ and $DCrO_2$ (see below) were refined separately by the least-squares technique. The results may be summarized as follows:

$HCrO_2$: The arrangement is insensitive to x_H over the range $0{\cdot}48 \le x_H \le 0{\cdot}50$. The thermal motion of H is much greater normal to the O–H–O bond than along it. Refinement with $x_H = 0{\cdot}50$ results in $x_O = 0{\cdot}4045 \pm 0{\cdot}0006$. O $\cdots$ O $= 2{\cdot}55 \pm 0{\cdot}02$ Å. Generalized agreement factor for the intensities (see below) $R_G = 0{\cdot}098$.

$DCrO_2$: The O–D–O bond is asymmetric with $x_D = 0{\cdot}4834 \pm 0{\cdot}0025$. The thermal parameters are not significantly different from zero. $x_O = 0{\cdot}4082 \pm 0{\cdot}0011$. O $\cdots$ O $= 2{\cdot}48 \pm 0{\cdot}03$ Å. O $\cdots$ D $= 1{\cdot}02 \pm 0{\cdot}04$ Å. $R_G = 0{\cdot}079$.

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† In other words, the O–D–O potential function is a symmetric double-minimum function.

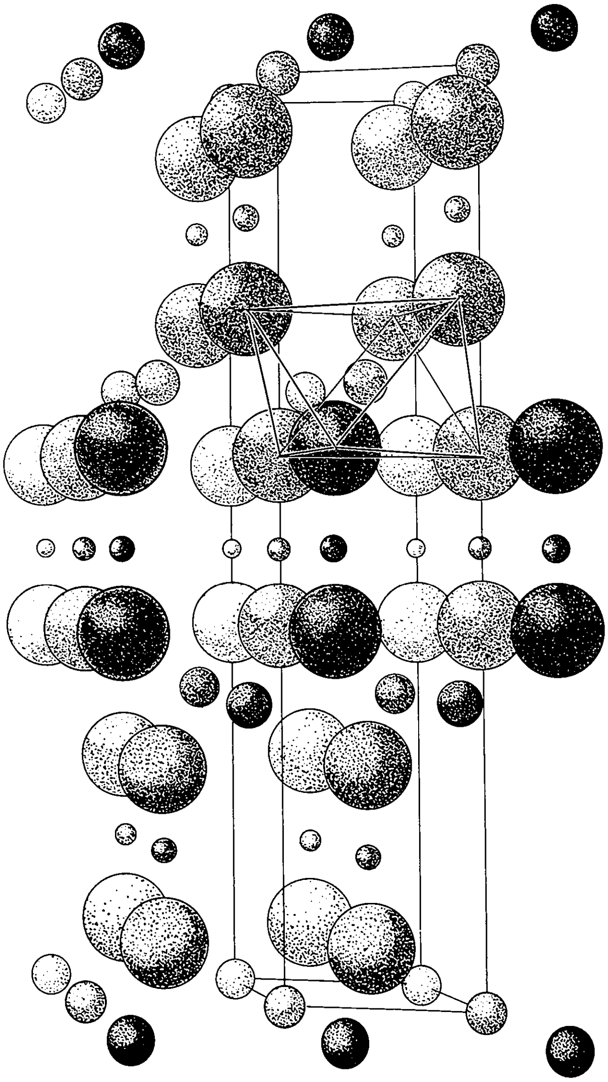

Fig. 1. The atomic arrangement in $HCrO_2$: Perspective view along the line ($x=\frac{1}{4}y$, $z=\frac{1}{2}$) from 40 Å of four hexagonal unit cells. The largest spheres are oxygen atoms; those of intermediate size are chromium; and the smallest are hydrogen, shown in the central position of the O–H–O bond. One of the CrO_6 octahedra is outlined.

The disturbing feature of these results is the apparent contraction of the O–H–O bond upon substitution of D for H. The hexagonal cell constants, as determined by us from an analysis of the X-ray powder patterns, are

$$\begin{aligned} HCrO_2&: a=2{\cdot}976\pm0{\cdot}001,\ c=13{\cdot}36\pm0{\cdot}01\ \text{Å}:\\ DCrO_2&: a=2{\cdot}983\pm0{\cdot}001,\ c=13{\cdot}50\pm0{\cdot}01\ \text{Å}.\end{aligned}$$

If one makes the very reasonable assumption that the substitution of D for H does not affect the Cr–O distance, then the above cell constants lead to an O–D–O bond length that is 0·06 Å *longer* than the O–H–O bond length. The results of the separate refinements, since they lead to the opposite order of bond lengths, are difficult to understand. Statistical tests of the difference between the O · · · O distances in the previous refinements indicate that the difference may not be significant. However, exact significance tests cannot be applied, mainly because the necessary hypotheses here are even less linear than in most crystallographic problems.

In this paper we present a new interpretation of these same neutron diffraction data, based on the simultaneous least-squares refinement of the two sets of data with the constraint that the Cr–O distance be the same in both compounds. Before discussing the results of this refinement, we describe the collection and treatment of the data.

Collection and treatment of the data

Polycrystalline samples of $HCrO_2$ and $DCrO_2$ were prepared and analyzed as described earlier (Snyder & Ibers, 1962). The neutron diffraction patterns were obtained on the apparatus described by Corliss, Hastings & Brockman (1953) with the samples in cylindrical aluminum sample holders about 18 mm in diameter. The powder patterns were corrected for background, but not for absorption, for although the linear absorption coefficient of $HCrO_2$ is high because of spin incoherence, the absorption correction for the sample geometry used is approximately isotropic.

Integrated intensities were derived from the data, and standard deviations in these intensities were estimated from the counting statistics and the uncertainty in the base levels of the peaks. Because of overlap, all peaks could not be resolved completely. Yet it was usually possible to estimate the relative contributions of the individual reflections to a multiple peak. Let T with estimated standard deviation $\sigma(T)$ be the total intensity of a multiple peak to which $A, B, \ldots$ contribute. Suppose that in some manner we estimate $k_A, k_B, \ldots$ such that

$$A=k_AT,\quad B=k_BT,\ \ldots\,.$$

Then with the assumption that the errors in the k's and T are uncorrelated we have

$$\begin{aligned}\sigma^2(A) &= \sigma^2(k_A)(T^2+\sigma^2(T))+k_A^2\sigma^2(T)\\ \varrho_{AB} &= k_Ak_B\sigma^2(T)\sigma^{-1}(A)\sigma^{-1}(B)\\ \varrho_{A,T-A} &= [k_A\sigma^2(T)-\sigma^2(A)]/[\sigma(A)\sigma(T-A)]\end{aligned}$$

where ϱ_{AB} is the correlation coefficient between A and B.* The individual estimates as well as the total intensity of a peak are included in the least-squares refinement of the data through the use of a weight matrix, which, since it takes into account these correlations, is non-diagonal. In this way we augment the limited number of completely resolved

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* It is not suggested that this is an adequate model for all overlapping peaks in all powder patterns.

intensities with estimates of the separate intensities in multiple peaks. Included in Table 1 are the values of the observed intensities together with the estimated standard deviations and the correlation coefficients used in the least-squares analysis.

Table 1. *Observed and calculated intensities for* $HCrO_2$ *and* $DCrO_2$*

Observation number	Reflections (rhombohedral indices)	$DCrO_2$			$HCrO_2$		
		I_o	I_c	$\sigma(I_o)$	I_o	I_c	$\sigma(I_o)$
1	111	0·2	0·2	0·2	54·4	52·1	0·8
2	100	78·1	74·6	1·5	9·9	4·2	1·4
3	110	90·3	86·1	1·4	16·5	11·6	1·9
4	222	0·2	0·6	0·5	22·0	16·1	3·0
5	211	0·6	0·2	0·3	17·9	23·5	3·5
6	221	21·3	24·3	2·0	90·2	104·5	5·7
7	322	3·7	5·6	0·6	31·4	36·4	2·0
8	$10\bar{1}+333$	78·1	80·7	1·0	31·2	31·4	2·0
9	210+332	5·2	8·1	0·6	26·7	29·4	2·1
10	$11\bar{1}$	21·9	19·8	3·4	0·9	1·7	0·9
11	200	21·9	24·8	4·1	3·2	4·3	1·6
12	321	—	—	—	33·1	28·9	3·9
13	$11\bar{1}+200+321$	46·3	46·0	1·7	—	—	—
14	433	27·4	27·7	6·9	18·9	23·6	3·4
15	311	8·8	10·6	3·0	42·8	41·6	5·3
16	220	—	—	—	7·2	7·6	6·6
17	220+433+311	51·7	38·4	3·2	—	—	—
18	444	10·0	2·8	2·3	—	—	—
19	444+443	16·6	8·3	3·0	5·7	11·4	5·8
20	432	3·3	5·8	2·3	—	—	—
21	331+432	3·3	8·9	2·3	15·3	18·2	6·4

Non-zero correlation coefficients used in the least-squares refinement

$DCrO_2$

(i,j)	$\varrho(i,j)$
18,19	0·77
20,21	0·94
10,11	0·04
10,13	0·24
11,13	0·20
14,15	0·08
14,17	0·24
15,17	0·18

$HCrO_2$

(i,j)	$\varrho(i,j)$
7,8	−0·71
11,12	0·07
11,14	0·05
11,15	0·07
11,16	−0·24
12,14	0·20
12,15	0·30
12,16	−0·54
14,15	0·19
14,16	−0·44
15,16	−0·52

* $I_c=\sum_i j(F_i^2/\sin\theta\sin 2\theta)\times 10^{24}\ \text{cm}^2$, where θ is the Bragg angle and j is the multiplicity.

Refinement of the combined data

Since we believe that substitution of D for H should not affect the Cr–O distance and since the separate refinements (Hamilton & Ibers, 1962) led to results at variance with this belief we chose to carry out another refinement in which the Cr–O distance is constrained to be the same in both compounds and the data from both compounds are refined simultaneously. The variable parameters are thus the two scale factors, the Cr–O distance, $B_{\parallel}$ (along the bond) and $B_{\perp}$ (normal to the bond) for H and for D, x_D, and x_H. (Temperature factors on the heavy atoms were set at zero, for in previous refinements where they were varied they reached values not significantly different from zero.) It is not possible to carry out the refinement with x_H as a variable parameter, for the matrix of the normal equations is singular for $x_H=0·50$, and is close enough to singularity at values of x_H near 0·50 to lead to spurious shifts in the refinement as a result of round-off errors and non-linearity. Rather it is necessary to carry out the refinement for fixed values of x_H.

Table 2 lists the results of the present series of refinements on x. Neutron scattering factors of 0·35, 0·58, −0·378, and 0·65 were used for Cr, O, H, D (Bacon, 1962). Again the results are insensitive to the value of x_H between about 0·485 and 0·50 and so no unequivocal statement can be made about the symmetry of the O–H–O bond. As opposed to the previous refinements the temperature factors on H do not differ significantly from zero. (A refinement based on the condition from the nuclear magnetic resonance study (Ibers, Holm & Adams, 1961), namely that for H $B_{\perp}-B_{\parallel}=4·7$ Å², led to essentially the same values of the geometrical parameters, but to slightly although not significantly worse overall agreement.) The O–H–O distance is 2·49 ± 0·02 Å. As in the previous refinements, the O–D–O bond is found to be asymmetric. The distances here are

Table 2. *Results of least-squares refinement on combined* $HCrO_2$ *and* $DCrO_2$ *data**

x_H Refined parameters	0·500		0·495	0·490	0·485	0·480	0·475
r(Cr–O)	1·979	±0·005	1·979	1·979	1·979	1·979	1·979
x_D	0·4767	±0·0026	0·4767	0·4767	0·4767	0·4768	0·4769
$B_{\parallel}$(H)	6·68	±5·32	6·32	5·21	3·19	0·11	−9·41
$B_{\perp}$(H)	1·58	±1·54	1·58	1·58	1·59	1·58	2·65
$B_{\parallel}$(D)	−3·15	±3·46	−3·15	−3·15	−3·15	−3·16	−2·97
$B_{\perp}$(D)	0·32	±0·80	0·33	0·33	0·33	0·33	0·36
R_G	0·0915		0·0915	0·0915	0·0916	0·0920	0·1129

Derived parameters		
x_O(H)	0·4068	±0·0008
x_O(D)	0·4056	±0·0008
r(O–D)	0·96	±0·04
$r(O\cdots D\cdots O)$	2·55	±0·02
$r(O\cdots H\cdots O)$	2·49	±0·02
$r(O\cdots O)$†(H)	2·61	±0·02
$r(O\cdots O)$†(D)	2·60	±0·02
$r(O\cdots O)$‡(H & D)	2·98	±0·005

* Standard deviations are those estimated for $x_H=\frac{1}{2}$; these were nearly independent of x_H, although they were of course proportional to the generalized R factor. The standard deviations in the scale factors are 2–3%.

† Distance from oxygen to oxygen related by symmetry operation $\bar{3}$.

‡ Distance from oxygen to oxygen related by symmetry operation 3. This is equal to the hexagonal cell constant a.

O–D = 0·96 ± 0·04 Å, O–D–O = 2·55 ± 0·02 Å; the temperature factors on D are not significantly different from zero. The O–O distances in the coordination octahedra are 2·60 ± 0·02 Å and 2·98 ± 0·005 Å, the octahedra being squashed along the threefold axis.

Table 1 lists the values of I (in barns) for these parameters ($x_H = 0{\cdot}50$). The agreement between calculated and observed I is judged from the generalized agreement factor

$$R_G = \left(\frac{\sum_{i,j} (I_o - I_c)_i w_{ij} (I_o - I_c)_j}{\sum_{i,j} (I_o)_i w_{ij} (I_o)_j} \right)^{\frac{1}{2}}$$

where w_{ij} are the elements of the weight matrix. The significance of the difference between the previous refinements of the separate data and the present combined refinement may be tested by use of the R_G in an analysis-of-variance test. Let R_0 be the value of R_G obtained in the previous refinement based on $n-m$ degrees of freedom. Let R_1 be the value of R_G for the corresponding intensity functions in the present refinement. Then, if the dimension of the hypothesis (the number of hypothesized parameter values) is b, the quantity

$$\left(\frac{R_1^2 - R_0^2}{b}\right)\left(\frac{R_0^2}{n-m}\right)^{-1}$$

may be tested for significance against tabulated percentage points $F(b, n-m, \alpha)$ of the usual analysis-of-variance distribution F (Hamilton, 1961). For neither the $HCrO_2$ nor the $DCrO_2$ data is the generalized R factor ratio significant at the very conservative significance level $\alpha = 0{\cdot}15$. The present refinement is thus not incompatible with the earlier ones and we prefer it because it is based on what we feel to be a more reasonable model.

The results of these significance tests are somewhat surprising when they are compared with the estimated standard deviations of the O · · · O distances in the earlier analysis. They thus provide a good example of the effects of non-linearities on statistical significance tests. It can be shown that the R factor ratio test is much less affected by non-linearities than are Student's t tests on the bond distances, and it is thus to be preferred. In comparing the R factors, we are comparing the agreement between the primary data and the calculations, whereas in making the usual significance tests on the parameters we are assuming a linear relationship, which may not exist, between the primary data and the parameters.

Conclusions

The neutron diffraction results here and previously (Hamilton & Ibers, 1962) are in complete agreement with the infrared results on the symmetry of the O–D–O bond in $DCrO_2$. The present results on $HCrO_2$ are compatible with both the previous nuclear magnetic resonance and infrared results, but they do not enable us to reach an unequivocal conclusion concerning the symmetry of the O–H–O bond. Even in cases where more plentiful and accurate data are available, from single-crystal studies (McGaw & Ibers, 1963), it has not been possible to get around the difficulties brought on by the smearing out of the scattering density as a result of zero-point energy vibrations.

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