The Crystal Structure of HCrO₂*

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A structure for HCrO₂ has been found in which one chromium(III) ion lies in $1(a)$ 0, 0, 0 and two oxygen ions in $2(c)$ $x, x, x; \bar{x}, \bar{x}, \bar{x}$ of space group $R\bar{3}m$. The single parameter x has been determined from powder data by trial-and-error to be 0.405 ± 0.003, with a residual factor R of 0.06 for resolved reflections not seriously affected by preferred orientation. The structure consists of distorted $(CrO_6)^{-9}$ octahedra, each sharing six of its edges with six surrounding coplanar octahedra to form continuous sheets in which the anions are close packed, lying parallel to the prominent {111} cleavage. This and certain other MX_2 structures containing sheets of linked octahedra differ from one another essentially only in the manner of superposition of successive sheets. In this structure the sheets are stacked so that oxygen ions of adjacent sheets are exactly superposed, hence the anions in the structure as a whole are only partly close packed. One hydrogen ion lies between each pair of superposed oxygen ions, this O–H–O distance being 2.55 ± 0.08 Å, in accord with infra-red absorption data. Symmetry indicates symmetrical hydrogen bonds, and in this respect the HCrO₂ structure appears unique among known isoformular structures.

Introduction

Fine-grained crystalline material of composition HCrO₂ has been encountered several times in studies of chromium oxide–water systems. Uninterpreted powder X-ray diffraction patterns, differential thermal analyses, a measured density and an approximate refractive index have been reported (Simon, Fischer & Schmidt, 1930; Laubengayer & McCune, 1952; Shafer & Roy, 1954). In the present investigation drusy aggregates of crystals up to several tenths of a millimetre across were available, prepared by thermal decomposition of aqueous chromic acid at 300 and 325° C. at elevated pressure (Thamer, Douglass & Staritzky, 1957). Quantitative chemical analysis of a sample of this material contaminated with chromium dioxide (CrO₂; cassiterite structure) gave by weight 61·0% chromium and, by the Penfield method, 9% water, to be compared with 61·18% and 10·60%, respectively, calculated for HCrO₂. On ignition this material formed green chromium sesquioxide (Cr₂O₃; identified by powder photographs), with a maximum observed weight loss of 9·5%.

Calibrated Weissenberg and precession photographs indicated Laue symmetry $\bar{3}m$ and gave hexagonal unit-cell dimensions $(\lambda(\text{Cu}K\alpha_1) = 1·54050$ Å, $\lambda(\text{Cu}K\alpha_2) = 1·54434$ Å, $\lambda(\text{Cu}K\beta_1) = 1·39217$ Å)

$$a_0 = 2·984 \pm 0·003 \text{ Å}, \quad c_0 = 13·40 \pm 0·01 \text{ Å};$$

cell volume 103·3 Å³; $c/a = 4·49$. Systematic absences were observed only for reflections with $-h+k+l \neq 3n$, indicating diffraction symbol $\bar{3}mR{-}{-}{-}$. The dimensions of this rhombohedral unit cell are

$$a_0 = 4·787 \pm 0·005 \text{ Å}, \quad \alpha = 36·3 \pm 0·1°;$$

cell volume 34·44 Å³. The density measured with the Berman balance using toluene was $4·11 \pm 0·03$ g.cm.⁻³ (five determinations), in agreement with a measured density of 4·12 g.cm.⁻³ reported by Laubengayer & McCune (1952). The density calculated for HCrO₂, assuming one formula unit per rhombohedral cell (formula weight 85·02; weight of unit atomic weight $1·6602 \times 10^{-24}$ g.), is 4·10 g.cm.⁻³. No piezoelectric effect was detected with an adaptation of the Stokes (1947) modification of the Giebe–Scheibe apparatus.

The crystals exhibit rhombohedron {101} and its complementary form {411}, unit rhombohedron {100}, prominent {111} cleavage, and twinning with {122} as twin plane. The crystals are dark brownish red in color and are optically uniaxial negative with refractive indices for sodium light $2·15_5$ for the ordinary ray, $1·97_5$ for the extraordinary ray; geometric mean index $2·09_3$; Lorentz–Lorenz refraction 11·0 cm.³. Shafer & Roy (1954) gave an approximate refractive index of $2·0 \pm 0·1$. The mean refractive index calculated for HCrO₂ from specific refractive energies (Larsen & Berman, 1934) is 2·1. The Lorentz–Lorenz refraction calculated for HCrO₂ from values for Cr₂O₃ (corundum structure), corundum (Al₂O₃) and diaspore (HAlO₂) is 10·9 cm.³.

Infra-red absorption spectrum

By Llewellyn H. Jones

Infra-red absorption spectra of HCrO₂ and of HAlO₂ (diaspore) were obtained from samples prepared as mineral oil mulls, as thin deposits of fine powder evaporated from an aqueous slurry on to silver chloride windows and as dispersions in potassium bromide discs.

For HCrO₂ there appeared no absorption bands in

the normal O–H stretching region, but there was a very broad band which started at about 2100 cm.$^{-1}$ and extended to about 1600 cm.$^{-1}$, with the center thus in the neighborhood of 1850 cm.$^{-1}$. If this broad band be attributed to O–H vibration in OHO groups this absorption frequency indicates, using the plot of Pimentel & Sederholm (1956), an oxygen–oxygen distance across the hydrogen bond of approximately 2·45 Å. An additional fairly strong band appeared at 1190 cm.$^{-1}$; this could be a hydrogen bonding frequency but more likely it arises from chromium–oxygen vibration.

A sample of HCrO$_2$ was heated with excess D$_2$O in a sealed tube at 200° C. for one week in an attempt to exchange D for H, but the spectrum of the product indicated no exchange.

Diaspore (HAlO$_2$) exhibits an absorption band at about 2900 cm.$^{-1}$, which very likely is due to O–H vibration in an OHO group. This frequency indicates, using the plot of Pimentel & Sederholm (1956), an oxygen–oxygen distance across the hydrogen bond of about 2·66–2·72 Å. The spectrum of HAlO$_2$ bore no resemblance to that of HCrO$_2$.

Determination of the chromium and oxygen coordinates

Assuming all equivalent positions of any set are fully occupied, one chromium(III) ion must be accommodated in one one-position set and two oxygen ions either in one two-position set or in two one-position sets per rhombohedral cell, neglecting for the present the one hydrogen ion. The one- and two-position sets of space groups embraced by diffraction symbol $\overline{3}mR$––– are (*International Tables*, 1952):

$R\overline{3}m$–D_{3d}^5: 1(*a*) 0, 0, 0. 1(*b*) $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$. 2(*c*) x, x, x; $\bar{x}, \bar{x}, \bar{x}$.
$R32$–D_3^7: Same as above.
$R3m$–C_{3v}^5: 1(*a*) x, x, x.

Lacking evidence to the contrary, the structure was assumed to be centrosymmetric, leaving only space group $R\overline{3}m$. Placing the chromium ion in either of the one-position sets leads to the same structure, and leaves only the one two-position set for the two oxygen ions. Thus the one chromium ion can be placed in 1(*a*) 0, 0, 0 and the two oxygen ions in 2(*c*) x, x, x; $\bar{x}, \bar{x}, \bar{x}$. As this structure contains only one parameter the expression for structure amplitude (*International Tables*, 1952) reduces to

$$F \propto f_{Cr+3} + 2f_{O-2} - 2\cos 2\pi x(h+k+l) \ .$$

The hydrogen ion need not enter this expression because of its negligible scattering power.

Scattering factors for Cr^{+3} were derived from those for Cr^0 by analogy with factors for other M^{+3} ions relative to those for M^0; factors for Cr^0 and O^{-2} were taken from *Internationale Tabellen* (1935). The tem-

perature factor was neglected in view of the limited angular range θ of the reflections considered. A set of observed structure amplitudes F_o (Table 1) was

Table 1. *Observed and calculated structure amplitudes*

hkl	F_o	F_c
111	41·9*	+22·2
100	7·3	7·5
110	22·1	20·5
222	12·5*	7·2
211	8·9	8·9
221	23·3	23·3
322	17·3	17·2
10$\bar{1}$	19·4 } †	20·2
333	8·8 }	9·2
210	12·0	14·4
332	13·9	13·3
11$\bar{1}$	8·9	7·7
200	13·2	14·2

* Reflections hhh are enhanced in intensity owing to preferred orientation in the powder sample arising from the prominent {111} cleavage.

† Unresolved in the powder photograph; F_o for these reflections are derived from partition of observed intensity in proportion to intensities calculated for the final parameter $x = 0.405$.

derived, after applying appropriate absorption, multiplicity, Lorentz and polarization factors (*Internationale Tabellen*, 1935; *International Tables*, 1952), from relative peak intensities above background obtained from densitometer measurements of a powder photograph*. The single-crystal photographs were not well suited for intensity measurements, and the powder data are ample for determination of the one parameter by trial and error.

Comparison of observed structure amplitudes (Table 1) with structure amplitudes calculated for different values of parameter x (Fig. 1) shows best agreement in the neighborhood of $x = 0.40$. Further trial-and-error refinement led to the final parameter $x = 0.405$, probably within ±0.003, yielding a residual factor $R = \Sigma||F_o|-|F_c|| \div \Sigma|F_o|$ of 0·16 including all reflections in Table 1 and 0·06 excluding unresolved reflections (10$\bar{1}$ and 333) and those seriously enhanced in intensity owing to preferred orientation (111 and 222). These acceptably small residual factors and the generally good agreement between observed and calculated structure amplitudes suggest that the chromium and oxygen coordinates proposed above are essentially correct.

Description of the structure and position of the hydrogen

The chromium and oxygen coordinates derived in the preceding section give a structure (Fig. 2) consisting

* Philips 114·6 mm. diameter powder camera; 0·2 mm. diameter glass capillary with walls 0·01 mm. thick; Cu $K\alpha$ radiation; Eastman Kodak Type A film for which density was calibrated as a function of exposure time. The complete powder pattern is given by Thamer *et al.* (1957).
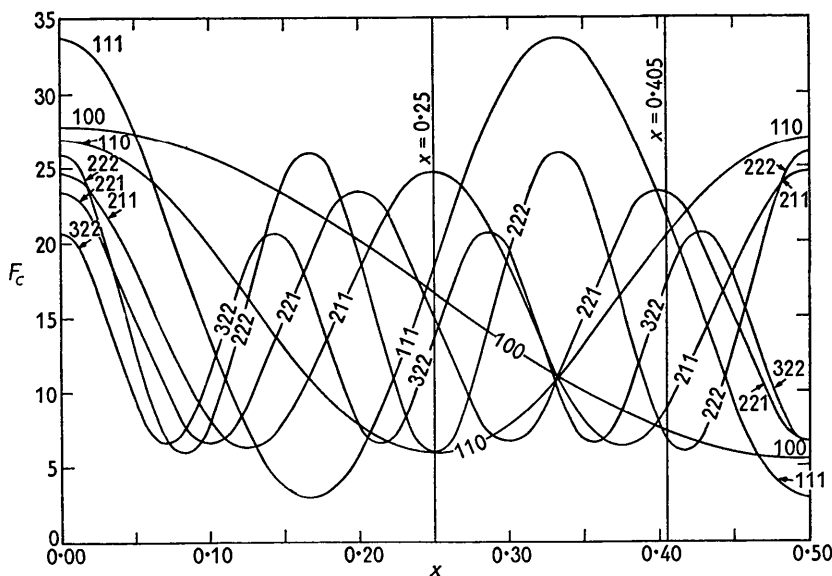
Fig. 1. Variation of calculated structure amplitudes with parameter x. Curves are symmetrical about $x = 0.50$.
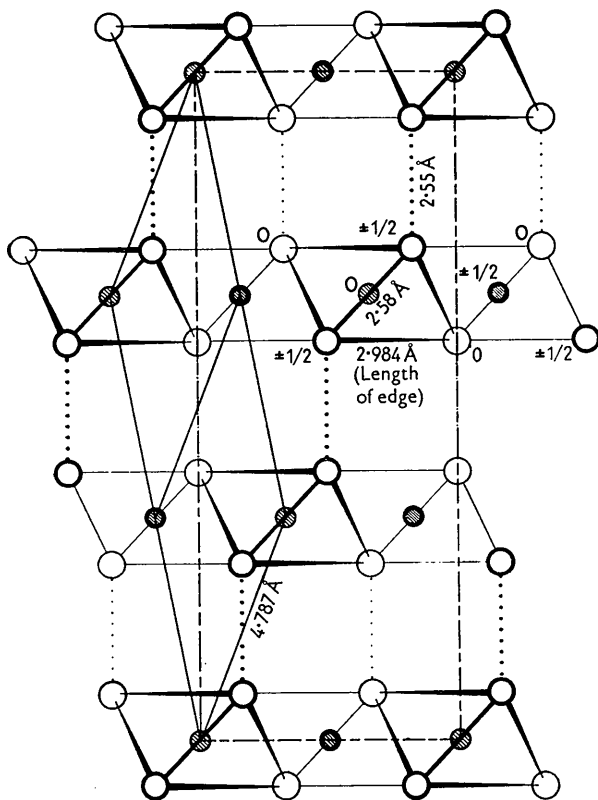

Fig. 2. Structure of $HCrO_2$ projected on $(10\bar{1})$. Larger, open circles represent oxygen ions, smaller, shaded circles chromium(III) ions, and dotted lines O–H–O bonds. Light circles represent ions in the plane of the paper, heavy circles ions one-half of an identity distance above and below the plane of the paper. $(CrO_6)^{-9}$ octahedra are outlined, and projected rhombohedral and corresponding hexagonal unit cells are indicated by solid and broken lines, respectively.

of oxygen ions at the vertices of deformed octahedra, with one chromium(III) ion at the center of each octahedron. The $(CrO_6)^{-9}$ octahedra thus formed lie with trigonal axes parallel to [111] and are compressed parallel to [111]. Each octahedron shares six of its edges with six surrounding coplanar octahedra to form continuous $(CrO_2)_n^{-n}$ sheets in which the anions are close packed, the sheets lying parallel to the prominent $\{111\}$ cleavage at $0, 0, 0$; $\frac{1}{3}, \frac{1}{3}, \frac{1}{3}$; $\frac{2}{3}, \frac{2}{3}, \frac{2}{3}$; etc. Between the octahedra in each sheet are deformed tetrahedra—right trigonal pyramids with equilateral bases parallel to $\{111\}$—alternately pointing upward and downward. The sheets are superposed so that an equilateral trigonal base of a tetrahedron in one sheet is exactly overlain by an equilateral trigonal side of an octahedron in the superjacent sheet, thus forming continuously linked, right equilateral trigonal prisms between the sheets. The anions of this structure are therefore only partly close packed.

The short oxygen–oxygen distances in this structure are as follows: (i) Between oxygen ions on the same side of a given sheet (i.e., unshared octahedral edges), six such distances per oxygen: 2.984 ± 0.003 Å $= a_0$ (hexagonal). (ii) Between oxygen ions on opposite sides of the same sheet (i.e., shared octahedral edges), three such distances per oxygen: 2.58 ± 0.06 Å. As to be expected, these shared octahedral edges are considerably shorter than the unshared edges (i) above (Pauling, 1948). (iii) Between superposed oxygen ions in adjacent sheets, one such distance per oxygen: 2.55 ± 0.08 Å. The significance of this distance will be considered later. There are six equal chromium–oxygen distances of 1.97 ± 0.04 Å. Taking 2.78 Å as the mean distance between oxygen ions in an octahedron gives a mean oxygen ion radius of 1.39 Å, a radius for the chromium(III) ion of 0.58 Å and a

radius ratio $r(Cr^{+3})/r(O^{-2})$ of 0·42. Pauling (1948) gave corresponding radii of 1·40 Å and 0·64 Å and a minimum radius ratio for stability of octahedral coordination of 0·414.

The disruption of anion close packing between adjacent $(CrO_2)_n^{-n}$ sheets, resulting from the superposition of oxygen ions in adjacent sheets, suggests, as pointed out by Pauling, that a hydrogen ion lies in twofold coordination between each pair of superposed oxygen ions. The hydrogen bonds thus formed satisfy the excess negative charge of the sheets and serve to hold them together. This O–H–O distance of 2·55±0·08 Å (distance (iii) above) is in accord with the approximate value 2·45 Å suggested by the infrared study, and corresponds to the 'short' (c. 2·55 Å) O–H–O bond (Wells, 1950). 'Short' O–H–O bonds are generally symmetrical owing to resonance of the hydrogen between two equivalent equilibrium positions lying between the oxygen ions (O–H $\cdots$ O $\rightleftharpoons$ O $\cdots$ H–O), each position about 1·0 Å from an oxygen ion (Pauling, 1948). In the HCrO$_2$ structure here proposed, based on space group $R\bar{3}m$, all oxygen ions are equivalent and have the same environment, hence no preferential attachment of the hydrogen ion is to be expected. This suggests symmetrical resonance of the hydrogen ion between the two equipoints of set $2(c)$ x, x, x; $\bar{x}, \bar{x}, \bar{x}$, with x near 0·48. Thus on the average the hydrogen ion would lie half-way between the sheets in position $1(b)$ $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. If the space group were $R3m$ the chromium and oxygen ions would lie in position $1(a)$ x, x, x; thus the oxygen ions would not all be equivalent, and the hydrogen ions could be preferentially attached to those of one kind, i.e., the O–H–O bonds could be unsymmetrical. However, there is no evidence that this is the case.

Related structures

Cadmium dichloride (CdCl$_2$) and a large number of isostructural MX_2 compounds (Pauling & Hoard, 1930) also crystallize in space group $R\bar{3}m$ and likewise contain one formula unit per rhombohedral cell with M in $1(a)$ $0, 0, 0$ and $2X$ in $2(c)$ x, x, x; $\bar{x}, \bar{x}, \bar{x}$; for cadmium dichloride $x = 36°\ 02'$ (cf. $\alpha = 36·3\pm0·1°$ for HCrO$_2$). However, in this case $x = 0·25$, resulting in a cubic-close-packed structure containing sheets of linked octahedra, rather than the partly close-packed sheet structure of HCrO$_2$. Neglecting the hydrogen ion, the two structures can be considered as derived from one another simply by turning each sheet of MX_6 octahedra over about $[2\bar{1}\bar{1}]$ without shifting its position. The parameter $x = 0·25$ of the cadmium dichloride type structures would thus become $x = 0·417$, not far from the value $x = 0·405$ found for HCrO$_2$. Indeed, the cell dimensions of HCrO$_2$ are such that a cadmium dichloride-type structure can be nicely fitted in. In this hypothetical structure, with $x =$

0·25, the oxygen ions lie in a cubic-close-packed arrangement and the $(CrO_6)^{-9}$ octahedra are much more regular than in the true structure, with oxygen–oxygen distances of 2·82 and 2·984 Å and chromium–oxygen distances of 2·05 Å.

The brucite, Mg(OH)$_2$, cadmium dichloride, CdCl$_2$, and HCrO$_2$ structures all belong to the same point group ($\bar{3}m$) and consist of sheets of linked MX_6 octahedra lying parallel to {0001}. These structures differ essentially only in the manner of superposition of these sheets. In the brucite structure (Aminoff, 1919; more recent summary by Wyckoff, 1951) successive sheets are exactly superposed with no displacement in {0001}. In the cadmium dichloride and HCrO$_2$ structures successive sheets are displaced in {0001} one-third of an identity distance parallel to [10$\bar{1}$0], the two different structures arising from displacement in opposite directions.

These relationships may be elucidated by listing the stacking sequence parallel to [0001] of the anion layers which make up the sheets of octahedra, two anion layers per sheet. For this purpose a layer with anions at $0, 0, 0, z$ (hexagonal coordinates) may be designated by 0 and the other layers by 1 or 2 according as they are displaced in {0001} $\frac{1}{3}$ or $\frac{2}{3}$ of an identity distance parallel to [10$\bar{1}$0]; intercalated cation layers may be designated by M. Thus:

For Mg(OH)$_2$ ($P\bar{3}m1$):

M M M M M
   1 2 1 2 1 2 1 2 etc.

Two anion layers (one sheet of octahedra) per unit cell, spaced evenly. Hexagonal close packing of anions.

For CdCl$_2$ ($R\bar{3}m$):

M M M M M
   1 0 2 1 0 2 1 0 etc.

Six anion layers (three sheets of octahedra) per unit cell, spaced evenly. Cubic close packing of anions.

For HCrO$_2$ ($R\bar{3}m$) (hydrogen bonds indicated by broken lines):

M M M M M
   $2 - - - 2$ $0 - - - 0$ $1 - - - 1$ $2 - - - 2$ etc.

Six anion layers (three sheets of octahedra) per unit cell, spaced unevenly owing to exact superposition of anions in adjacent sheets of octahedra. Discontinuous close packing of anions.

Related compounds

Crystal structures of phases having composition $RO(OH)$ or HRO_2 have been reported for the following cations R^{+3}:

Al (diaspore)†, Mn (groutite)†, Fe (goethite)†, Ga‡: α phase $(Pbnm)$.—This structure contains 'long' O–H–O bonds $(2\cdot71\pm0\cdot05$ Å in diaspore*), and the oxygen ions, in two four-position sets, do not all have the same environment although all participate in O–H–O bonding. These features suggest unsymmetrical (hydroxyl) rather than symmetrical O–H–O bonds (Wells, 1950). Thus the formula could be written ROOH.

Al (boehmite)†, Fe (lepidocrocite)†, $(Ga_xAl_{(1-x)})$ with x between 0 and $0\cdot3\S$: γ phase $(Amam)$.—This structure contains oxygen ions in two four-position sets which play quite different roles. Each oxygen ion of one set is bonded to four R^{+3} ions only. Each oxygen ion of the other set is bonded to only two R^{+3} ions and forms one 'long' O–H–O bond $(2\cdot70\pm0\cdot05$ Å in lepidocrocite) with each of two other oxygen ions of the same set; these bonds are unsymmetrical, each of these oxygen ions thus forming a directed hydroxyl bond (Wells, 1950). Hence the formula could be written RO(OH).

Mn (manganite) $(B2_1/d)\|$.—This structure apparently contains 'long' O–H–O bonds $(2\cdot65$ Å), and the oxygen ions, in two eight-position sets, do not all have the same environment although all participate in O–H–O bonding. As in the case of the dimorphous α phase described above, these features suggest unsymmetrical (hydroxyl) rather than symmetrical O–H–O bonds, and the formula could be written ROOH.

Cr $(R\bar{3}m)$.—This structure contains 'short' O–H–O bonds $(2\cdot55\pm0\cdot08$ Å), and all oxygen ions are equivalent and have the same environment, suggesting symmetrical O–H–O bonds. Hence the formula could be written ROHO or HRO$_2$.

Other isoformular crystalline phases have been reported for R^{+3} = Sc, Mn (β phase), Fe (β phase, of uncertain relation to Mn β phase), Co (stainierite), In, La, Pr, Er and Yb. However, the physical properties reported are too scanty to establish with certainty the structural identity of any of these phases with any of the four structures described above or with each other.

Thus the HCrO$_2$ structure would seem unique among the four isoformular structures which are known, in that the O–H–O bonds are 'short' and appear to be symmetrical.

The anions in the α-ROOH and manganite structures have been described as almost perfectly hexagonal close packed (Wyckoff, 1951). However, the discontinuous anion close packing in HCrO$_2$ does not result in a much more open structure, as revealed by comparison of volumes per oxygen in these structures:

	α		γ
Al	$14\cdot6$ Å^3		$16\cdot0$ Å^3
Fe	$17\cdot7$		$18\cdot6$
Mn		$16\cdot6$ Å^3	
Cr		$17\cdot2$	
Close-packed spheres of radius $1\cdot40$ Å		$15\cdot5$	

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† Data have been summarized by Wyckoff (1951).
‡ The latest paper is that of Roy, Hill & Osborn (1952).
* The infra-red study of Jones (see above) indicated about $2\cdot66$–$2\cdot72$ Å.
§ Hill, Roy & Osborn (1952).
‖ The latest paper describing the structure is that of Buerger (1936).

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