

**THE DETERMINATION OF CRYSTAL STRUCTURE OF CHROMIUM(II) PHOSPHITE DIHYDRATE,  $\text{CrHPO}_3 \cdot 2 \text{H}_2\text{O}$** Jiří BRYNDA<sup>a</sup>, Bohumil KRATOCHVÍL<sup>b\*</sup> and Ivana ČISAŘOVÁ<sup>c</sup><sup>a</sup> *Department of Inorganic Chemistry,  
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The crystal structure of  $\text{CrHPO}_3 \cdot 2 \text{H}_2\text{O}$  has been solved by the heavy atom method. The compound crystallizes in the orthorhombic space group  $P2_12_12_1$  with the unit cell parameters  $a = 679.25(8)$ ,  $b = 915.61(8)$ ,  $c = 752.2(1)$  pm,  $Z = 4$ . The structure was refined to the final reliability factor  $R = 0.043$  for 1 040 observed reflexions ( $I > 1.96\sigma(I)$ ). The structure consists of chains formed by  $\text{CrO}_6$  octahedra connected each other in vertices. The chains are interconnected by phosphite tetrahedra  $\text{HPO}_3$ . Hydrogen bridges of water-phosphite tetrahedron and water-water types form space cross-linking of the whole structure. Bond distances Cr—O in the tetragonally distorted octahedron range from 201.2 to 304.9 pm. The interatomic distances P—O in phosphite tetrahedron are between 152.1 and 152.7 pm. The degree of the distortion DISQ of  $\text{HPO}_3$  tetrahedron and  $\text{CrO}_6$  octahedron is discussed on the basis of known structures of phosphites and chromium(II) compounds.

Isolated or condensed phosphite anions can be formally derived by a subsequent elimination of fractions  $1/2 \text{H}^+$  and/or  $1/2 \text{H}_2\text{O}$  from the formula unit of phosphorous acid,  $\text{H}_3\text{PO}_3$ . A number of these anions were actually found in the crystal structures of phosphites. The crystallochemistry of inorganic phosphites has been recently worked out<sup>1</sup>.

Chromium(II) phosphite dihydrate crystallizes from solution after substitution of two cations  $\text{H}^+$  by  $\text{Cr}^{2+}$ . The structure of an analogous copper compound,  $\text{CuHPO}_3 \cdot 2 \text{H}_2\text{O}$ , was determined by Handlovič<sup>2</sup>. Ebert and Kavan<sup>3</sup> predicted that  $\text{CuHPO}_3 \cdot 2 \text{H}_2\text{O}$  and  $\text{CrDPO}_3 \cdot 2 \text{H}_2\text{O}$  are isostructural. The study of the crystal structure of  $\text{CrHPO}_3 \cdot 2 \text{H}_2\text{O}$ , which is the aim of this work, is interesting from two points of view. First, for completion of our knowledge of the bonding possibilities of phosphite tetrahedron in crystallochemistry of inorganic phosphites, and secondly, for unusual stabilization of divalency of chromium in this structure. There are not many compounds containing Cr(II) having the structure described in literature — only  $\text{Cr}_2(\text{CH}_3\text{COO})_4 \cdot 2 \text{H}_2\text{O}$  (ref.<sup>4</sup>) of oxo-compounds and halogenides  $\text{CrX}_2$ , where  $\text{X} = \text{F}$  (ref.<sup>5</sup>),  $\text{Cl}$  (ref.<sup>6</sup>),  $\text{Br}$  (ref.<sup>7</sup>), and  $\text{I}$  (refs.<sup>8,9</sup>) of others.

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## EXPERIMENTAL

Chromium(II) phosphite dihydrate was prepared according to Ebert and Podlaha<sup>10</sup> by the reaction of chromium(II) acetate with phosphorous acid. The crystals of the title compound were decanted by water, acetone and then dried freely in air. Phosphorus was determined gravimetrically as  $\text{Mg}_2\text{P}_2\text{O}_7$  and chromium by chelatometry. For  $\text{CrHPO}_3 \cdot 2 \text{H}_2\text{O}$  (168·01) calculated: 30·95% Cr, 18·44% P; found: 30·85% Cr, 18·50% P. The density of crystals was measured by flotation in a mixture of methane diiodide and toluene under 293 K.

Preliminary values of the unit cell parameters and the systematic extinction of reflexions were determined from the Weissenberg photographs  $h00$ :  $h = 2n + 1$ ,  $0k0$ :  $k = 2n + 1$ ,  $00l$ :  $l = 2n + 1$ . The measured crystal was ground to a spherical shape ( $r = 0\cdot05$  mm). The measurement was made with a four circle diffractometer Hilger & Watts at 293 K with  $\text{MoK}_\alpha$  radiation,  $\lambda = 71\cdot069$  pm, filtered by Zr filter. The final unit cell parameters were refined from the set of 25 centered high-angle reflexions. Total of 1 197 symmetrically independent reflexions were measured in the range  $0^\circ < 2\theta < 66^\circ$  by the learnt profile method<sup>11</sup>. No significant changes were observed in the intensities of three standard reflexions during the measurement. Total of 1 040 reflexions were signed as observed according to the criterion  $I > 1\cdot96\sigma(I)$  and the remaining 157 reflexions were excluded from the refinement. The absorption correction was neglected ( $\mu r = 0\cdot13$ ). The phase problem was solved by the heavy atom method and the positions of hydrogen atoms were found from the difference synthesis. The structure refinement was made by minimization of the sum  $\sum w(|F_o| - |F_c|)^2$  using the full-matrix least-squares method. The positions of hydrogen atoms could not be refined. They were fixed with the isotropical temperature factors corresponding to their bonding partners. The final values of reliability factors\* are:  $R = \sum \Delta / \sum |F_o| = 0\cdot043$ ,  $R_w = [\sum w\Delta^2 / \sum w|F_o|^2]^{1/2} = 0\cdot043$  for 1 040 observed reflexions and the weighing scheme is  $w = 2\cdot507 / [\sigma^2(F_o) + 0\cdot00013|F_o|^2]$ . The highest maximum on the final difference map is  $0\cdot9e / (100 \text{ pm})^3$ . The scattering factor for chromium was taken from the International Tables<sup>12</sup>. The calculations were made using programs SHELX76 (ref.<sup>13</sup>) and TLS (ref.<sup>14</sup>) with computers ICL 4-72, Siemens 7536 and M7000.

## RESULTS AND DISCUSSION

The basic crystallographic data for the title compound are given in Table I. The final fractional coordinates and the parameters of temperature vibrations are given in Table II. The projection of the structure along the  $c$  axis is in the Fig. 1. The

TABLE I

The basic crystallographic data for  $\text{CrHPO}_3 \cdot 2 \text{H}_2\text{O}$

$a = 679\cdot25(8)$ pm	$D_c = 2\cdot385$ g cm <sup>-3</sup>
$b = 915\cdot61(8)$ pm	$D_o = 2\cdot340(20)$ g cm <sup>-3</sup>
$c = 752\cdot2(1)$ pm	Space group $P2_12_12_1$
$V = 467\cdot8(9) \cdot 10^6$ pm <sup>3</sup>	$\mu(\text{MoK}_\alpha) = 2\cdot56$ mm <sup>-1</sup>
$Z = 4$	$F(000) = 336$

\* The values of observed and calculated structure factors and anisotropic temperature factors (deposited with the second author) will be sent on request.

TABLE II

Final coordinates of atoms ( $\cdot 10^4$  for non-hydrogen atoms and  $\cdot 10^3$  for hydrogens) and their temperature parameters ( $U_{\text{eq}} = 1/3(U_{11} + U_{22} + U_{33})$  for non-hydrogen atoms and  $U_{\text{iso}}$  for hydrogens). Estimated standard deviations are given in parentheses

Atom	$x/a$	$y/b$	$z/c$	$U_{\text{eq}}, U_{\text{iso}} (\cdot 10^4 \text{ pm}^2)$
Cr	5 162(1)	1 585(1)	2 205(1)	123(3)
P	2 651(2)	1 005(1)	5 700(2)	112(4)
O(1)	2 496(5)	2 122(4)	7 189(5)	167(13)
O(2)	4 654(5)	1 080(4)	4 774(5)	152(14)
O(3)	2 292(6)	-545(4)	6 377(5)	159(17)
O(4)	5 456(6)	2 254(4)	9 602(5)	210(17)
O(5)	2 875(7)	4 378(5)	3 008(7)	305(21)
H(P)	141	119	442	500
H(41)	471	230	886	700
H(42)	590	291	992	700
H(51)	248	387	205	950
H(52)	164	473	385	950

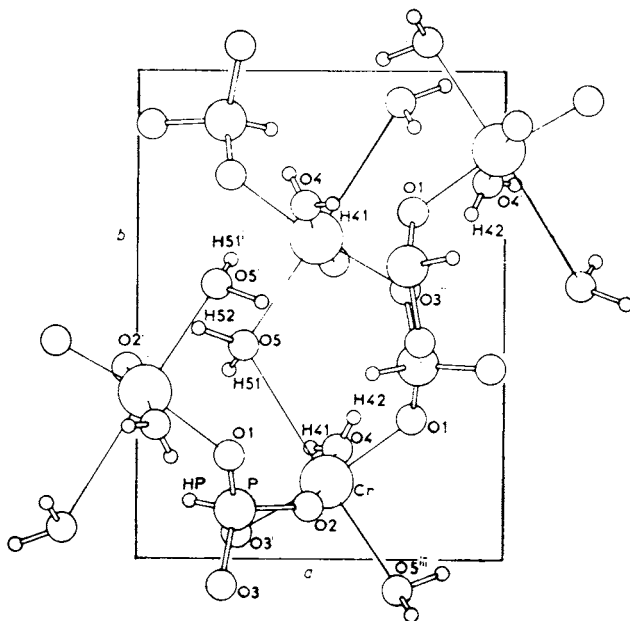


FIG. 1

The crystal structure of  $\text{CrHPO}_3 \cdot 2 \text{H}_2\text{O}$

crystal structure of  $\text{CrHPO}_3 \cdot 2 \text{H}_2\text{O}$  is formed by infinite chains of the tetragonally distorted octahedra  $\text{CrO}_3(\text{H}_2\text{O})_3$  interconnected by vertices occupied by two oxygen atoms O(5) of water molecules. The four remaining coordination sites in every octahedron are occupied by oxygens of phosphite anions O(1), O(2), O(3) and the oxygen of crystal water O(4). Chains of octahedra (parallel to  $b$  axes) are interconnected by  $\text{HPO}_3^{2-}$  anions, so that each oxygen atom in the coordination sphere of the chromium ion corresponds to three different phosphite anions. However, a single phosphite anion does not connect three different chains. Two oxygen atoms are bonded to two subsequent chromium atoms in one chain and the third oxygen atom is bonded to the adjacent Cr chain. In addition to the bridging molecules of crystal water, the chromium octahedron contains one molecule of non-bridging water. Hydrogen atoms of the non-bridging molecule of water, H(41), H(42), form hydrogen bonds to two different phosphite anions. Also, hydrogens of the bridging water molecule form hydrogen bonds: H(51) is bonded to O(4) and H(52) to O(2) of the phosphite anion.

The structure  $\text{CrHPO}_3 \cdot 2 \text{H}_2\text{O}$  is isostructural with  $\text{CuHPO}_3 \cdot 2 \text{H}_2\text{O}$ . A comparison of unit cell parameters of the chromium salt with the copper salt ( $a = 671$ ,  $b = 900$ ,  $c = 740$  pm) shows a small expansion of the unit cell in favour of  $\text{CrHPO}_3 \cdot 2 \text{H}_2\text{O}$ . Also, the corresponding bond distances M—O are higher (on the average) for the chromium salt (226.5 pm; Table III) than for the copper salt (221.6 pm). The dif-

TABLE III

Interatomic distances (in pm) and angles (in  $^\circ$ ). Symmetry codes: i)  $1/2 - x, -y, 1/2 + z$ ; ii)  $1/2 + x, 1/2 - y, -z$ ; iii)  $-x, 1/2 + y, 1/2 - z$

The chromium atom environment					
Cr—O1 <sup>ii</sup>	201.7(3)	O3 <sup>i</sup> —Cr—O2	92.7(2)	O1 <sup>ii</sup> —Cr—O4	88.0(2)
Cr—O2	202.5(3)	O3 <sup>i</sup> —Cr—O1 <sup>ii</sup>	171.6(2)	O1 <sup>ii</sup> —Cr—O5 <sup>iii</sup>	94.3(3)
Cr—O3 <sup>i</sup>	201.2(4)	O3 <sup>i</sup> —Cr—O4	85.8(2)	O1 <sup>ii</sup> —Cr—O5	82.0(3)
Cr—O4	206.1(4)	O3 <sup>i</sup> —Cr—O5 <sup>iii</sup>	92.1(3)	O4—Cr—O5 <sup>iii</sup>	97.6(3)
Cr—O5	304.9(6)	O3 <sup>i</sup> —Cr—O5	92.3(3)	O4—Cr—O5	89.3(3)
Cr—O5 <sup>iii</sup>	242.3(6)	O2—Cr—O1 <sup>ii</sup>	92.9(2)	O5 <sup>iii</sup> —Cr—O5	172.1(3)
		O2—Cr—O4	174.2(2)		
		O2—Cr—O5 <sup>iii</sup>	88.0(3)		
		O2—Cr—O5	85.2(3)		
The phosphorus atom environment					
P—O1	152.5(4)	H(P)—P—O2	114.6	O2—P—O1	111.5(2)
P—O2	152.1(4)	H(P)—P—O1	103.4	O2—P—O3	111.6(2)
P—O3	152.7(4)	H(P)—P—O3	105.6	O1—P—O3	109.6(2)
P—H(P)	128.8				

ference found, 4.9 pm, is in agreement with the fact that the difference between the ion radii of cations  $\text{Cr}^{2+}$  and  $\text{Cu}^{2+}$  is 7 pm;  $r_{\text{Cr}^{2+}} = 94$ ,  $r_{\text{Cu}^{2+}} = 87$  pm for the coordination number six (ref.<sup>15</sup>). Comparing the P—O bonds, the average bond length is higher in the chromium salt by 1.5 pm than in the copper salt. The individual distances P—O in  $\text{CrHPO}_3 \cdot 2\text{H}_2\text{O}$  differ by 0.9, 0.7, and 0.3 pm from the average value 151.8 pm of the P—O bonds in all other phosphites containing isolated  $\text{HPO}_3^{2-}$  anions (ref.<sup>1</sup>).

The degree of geometrical distortion can be evaluated by the index DISQ defined by<sup>16</sup>

$$\text{DISQ} = \sum_{m=1}^n (P - A_m)^2 / (nP^2), \quad (1)$$

where  $P$  is the average value corresponding to the maximum possible symmetry,  $A_m$  are the individual values, and  $n$  is their number. The index DISQ is  $2.1 \cdot 10^{-5}$  for bond distances P—O and  $1.2 \cdot 10^{-4}$  for angles O—P—O in  $\text{CrHPO}_3 \cdot 2\text{H}_2\text{O}$ . From the point of view of bond distances, the phosphite tetrahedron in  $\text{CrHPO}_3 \cdot 2\text{H}_2\text{O}$  is only little distorted; from the point of view of bond angles, it is distorted usually with respect to other phosphite tetrahedra under study. The evaluation of distortion of the octahedron  $\text{CrO}_6$  in  $\text{CrHPO}_3 \cdot 2\text{H}_2\text{O}$  is more difficult because there are no suitable data for comparison. In the structure  $\text{Cr}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$  the group  $\text{CrO}_6$  cannot be described as octahedron because it is formed by two tetragonal pyramids<sup>4</sup> connected by two bridges formed by carboxyl groups. The oxygen atoms of water molecules are placed in vertices of the pyramids. The bonding interaction is also between chromium atoms. Comparing the equatorial bonds Cr—O, the average length is by 6 pm shorter for acetate than for  $\text{CrHPO}_3 \cdot 2\text{H}_2\text{O}$ . The average octahedron  $\text{CrX}_6$  was taken as a basis for the calculation of the distortion index for octahedron  $\text{CrO}_6$  in chromium(II) phosphite. The distorted octahedron has the point symmetry  $\bar{1}$  in halides; only in the orthorhombic  $\text{CrI}_2$  has the point symmetry  $I$ , similarly to the octahedron  $\text{CrO}_6$  in  $\text{CrHPO}_3 \cdot 2\text{H}_2\text{O}$ . The value of the index DISQ is 0.028 for Cr—O distances and 0.002 for angles O—Cr—O in the compound under study.

TABLE IV

Interatomic distances O...O (in pm) and angles O—H...O (in °) in hydrogen bonds

$\text{O4}^{\text{iii}} \dots \text{O1}^{\text{iii}}$	271.1(5)	$\text{O4}^{\text{iii}} - \text{H41}^{\text{iii}} \dots \text{O1}^{\text{iii}}$	170.2
$\text{O4}^{\text{i}} \dots \text{O3}^{\text{ii}}$	263.5(5)	$\text{O4}^{\text{i}} - \text{H42}^{\text{i}} \dots \text{O3}^{\text{ii}}$	156.3
$\text{O5}^{\text{i}} \dots \text{O4}^{\text{iii}}$	296.4(6)	$\text{O5}^{\text{i}} - \text{H51}^{\text{i}} \dots \text{O4}^{\text{iii}}$	156.2
$\text{O5} \dots \text{O2}^{\text{ii}}$	278.3(6)	$\text{O5} - \text{H52} \dots \text{O2}^{\text{ii}}$	139.6

Both octahedra,  $\text{CrO}_6$  in  $\text{CrHPO}_3 \cdot 2 \text{H}_2\text{O}$  and  $\text{CuO}_6$  in  $\text{CuHPO}_3 \cdot \text{H}_2\text{O}$ , are tetrahedrally distorted due to the Jahn–Teller effect. A special feature of the distortion is a substantial irregularity in the prolongation of the axial bonds Cr—O, resp. Cu—O (242.3 and 304.9 pm in  $\text{CrO}_6$  and 234.9 and 303.6 pm in  $\text{CuO}_6$ ). A similar asymmetric tetragonal distortion of octahedron was also found in  $\text{CuSeO}_3 \cdot 2 \text{H}_2\text{O}$  (ref.<sup>17</sup>) and  $\text{CuTeO}_3 \cdot 2 \text{H}_2\text{O}$  (ref.<sup>18</sup>).

Four types of hydrogen bonds involving only hydrogen atoms of crystal water molecules were found in the title compound  $\text{CrHPO}_3 \cdot 2 \text{H}_2\text{O}$ . Three hydrogen bridges connect water molecules with oxygens of phosphite anions. The fourth hydrogen bond connects the molecules of crystal water. Interatomic distances  $\text{O} \cdots \text{O}$  and angles  $\text{O}—\text{H} \cdots \text{O}$  of hydrogen bonds are given in Table IV and are in a good agreement with the corresponding values summarized for phosphites in ref.<sup>1</sup>.

As shown in Fig. 1, the structure  $\text{CrHPO}_3 \cdot \text{H}_2\text{O}$  is formed by chains of octahedra  $\text{CrO}_6$ , which are connected together in opposite vertices. These octahedra are linked with tetrahedra  $\text{HPO}_3$ , both in the direction of chains and in the direction perpendicular to the chains. Moreover, the whole structure is interconnected by a three-dimensional network of hydrogen bonds. This “polymer” ordering of the structure is evidently the main reason for the stabilization of divalency of chromium atom in  $\text{CrHPO}_3 \cdot 2 \text{H}_2\text{O}$ .

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