

## The Crystal Structure of Calcium Dichromate Bis(hexamethylenetetramine) Heptahydrate

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The structure of  $\text{Cr}_2\text{O}_7\text{Ca} \cdot 2[(\text{CH}_2)_6\text{N}_4] \cdot 7\text{H}_2\text{O}$  has been determined by Patterson and Fourier methods and refined by full-matrix least-squares computations to a final  $R$  of 0.036 for 2961 independent non-zero reflexions. The crystals are monoclinic, space group  $C2/c$ , with  $a = 14.013$  (6),  $b = 14.384$  (6),  $c = 13.362$  (6) Å,  $\beta = 103.03$  (7)°,  $Z = 4$ . The structure is characterized by hydrogen bonds between the heptahydrate polyhedron around the calcium atom and the dichromate ion as well as the hexamethylenetetramine molecules.

### Introduction

This work was undertaken as part of a structural study of hydrogen-bonded substances. Among the many compounds formed by hexamethylenetetramine (HMT) with different inorganic salts, the X-ray structure of calcium dichromate HMT heptahydrate is reported after that of magnesium dichromate HMT hexahydrate (Dahan, 1974) to compare the geometries of the hydration polyhedra and the hydrogen-bonding systems around magnesium and calcium.

### Experimental

Calcium dichromate HMT heptahydrate was first crystallized by Debucquet & Velluz (1933). Following their instructions, crystals were grown from the mixture of two warm aqueous solutions of  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{CaCl}_2$ , and of HMT. The orange-coloured prismatic crystals were washed with acetone after standing overnight. The density was determined by flotation in a mixture of carbon tetrachloride and bromoform, and was in good agreement with the calculated value.

The intensities were collected in the Philips Research Laboratories on a Philips PW1100 computer-controlled four-circle diffractometer in the  $\omega$ -scan mode (scan width = 1.46°, scan speed = 0.030 s<sup>-1</sup>).

4022 reflexions up to  $2\theta = 61^\circ$  were measured. Three reference reflexions were recorded after each sequence of 70 measured reflexions and remained constant to within  $\pm 1\%$ .

With  $I \leq 2\sigma(I)$ , 788 reflexions were omitted as unobserved. Standard deviations  $\sigma(I)$  were calculated from

$$\sigma(I) = (I_1 + I + I_2)^{1/2}$$

where  $I_1$  and  $I_2$  are the background counts and  $I$  the peak count.

132 other reflexions were absent due to systematic extinction and 141 were redundant due to space-group equivalence. The remaining 2961 reflexions were all used in the structural determination.

Table 1. Crystal data

Formula	$\text{Cr}_2\text{O}_7\text{Ca} \cdot 2[(\text{CH}_2)_6\text{N}_4] \cdot 7\text{H}_2\text{O}$
M.W.	662
Space group	$C2/c$
Equivalent positions	i $x, y, z$ ; ii $-x, -y, -z$ ; iii $-x, y, \frac{1}{2}-z$ ; iv $x, -y, \frac{1}{2}+z$ ; v $\frac{1}{2}+x, \frac{1}{2}+y, z$ ; vi $\frac{1}{2}-x, \frac{1}{2}-y, -z$ ; vii $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ ; viii $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$ .
Lattice constants	$a = 14.013$ (6), $b = 14.384$ (6), $c = 13.362$ (6) Å $\beta = 103.03$ (7)°, $U = 2624$ Å <sup>3</sup> , $Z = 4$
Density	$D_m = 1.70$ , $D_x = 1.676$ g cm <sup>-3</sup>
Linear absorption coefficient	$\mu = 11.2$ cm <sup>-1</sup> ( $\lambda = 0.7107$ Å)

The crystal data are given in Table 1.

The data were corrected for Lorentz and polarization effects but not for absorption.

### Structure determination

Knowing that the calcium atom was in a special position, the Cr and Ca atoms were easily located from a Patterson function. A structure-factor calculation based on the coordinates of these atoms gave an  $R$  ( $= \sum ||F_o| - |F_c|| / \sum |F_o|$ ) of 0.38. A Fourier map phased on the heavy-atom coordinates resulted in the location of all nonhydrogen atoms. All calculations were performed on an IBM 370-165 computer.

Scattering factors were those for  $\text{Cr}^{3+}$ ,  $\text{Ca}^{2+}$  and  $\text{O}^-$  for the calcium dichromate, and those for neutral atoms for C, N, O and H of the HMT and water molecules. They were taken from *International Tables for X-ray Crystallography* (1962).

A full-matrix least-squares calculation, with the local version *SIRIUS IV* of the program *ORFLS* (Busing, Martin & Levy, 1962), was used to refine the atomic coordinates and isotropic temperature factors of all non-hydrogen atoms.  $R$  fell to 0.11 and was reduced to 0.055 by anisotropic refinement.

All hydrogen atoms were located from a difference synthesis. The refinement of their coordinates (the isotropic thermal parameters were those of the atoms to which they are bonded) resulted in an  $R$  of 0.038.

Table 2. Fractional atomic coordinates ( $\times 10^5$ ) and thermal parameters ( $\times 10^5$ ) in the form  $T = \exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ Estimated standard deviations ( $\times 10^5$ ) are in parentheses.

$$B(\text{\AA}^2) \text{ is } \frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + 2\beta_{12}ab \cos \gamma + 2\beta_{13}ac \cos \beta + 2\beta_{23}bc \cos \alpha).$$

	$x/a$	$y/b$	$z/c$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	$B$
Cr	8146 (3)	28384 (3)	18403 (3)	308 (2)	276 (2)	361 (2)	59 (1)	145 (2)	24 (2)	2.26
O(B)	0	23099 (20)	25000	709 (21)	345 (15)	951 (27)	0	561 (20)	0	4.44
O(1)	8547 (22)	21953 (18)	8753 (19)	1011 (21)	605 (15)	647 (16)	92 (14)	412 (15)	-152 (13)	5.39
O(2)	18794 (17)	29015 (21)	25696 (19)	443 (13)	1001 (21)	673 (16)	-9 (13)	33(12)	23 (16)	5.48
O(3)	4270 (20)	38431 (16)	14261 (21)	849 (18)	385 (11)	958 (21)	195 (12)	436 (16)	210 (12)	5.07
Ca	0	71408 (4)	25000	230 (3)	204 (2)	287 (3)	0	57 (2)	0	1.78
O'(1)	6730 (15)	85361 (13)	19033 (15)	506 (11)	312 (9)	459 (12)	-88 (8)	211 (9)	29 (8)	3.04
O'(2)	16466 (13)	69481 (14)	32908 (17)	268 (9)	351 (10)	648 (14)	7 (7)	11 (9)	169 (9)	3.20
O'(3)	3584 (17)	67197 (17)	8943 (15)	550 (13)	646 (14)	328 (11)	203 (11)	113 (10)	-46 (10)	3.87
O'(4)	0	54575 (20)	25000	838 (25)	250 (13)	617 (23)	0	180 (19)	0	4.15
N(1)	34165 (15)	48066 (15)	13757 (15)	388 (11)	312 (12)	342 (12)	58 (9)	85 (9)	60 (9)	2.59
N(2)	35993 (17)	57375 (14)	-972 (16)	495 (13)	244 (9)	364 (12)	-75 (9)	99 (10)	-8 (8)	2.72
N(3)	24166 (15)	44648 (14)	-3385 (16)	335 (10)	285 (9)	398 (12)	-36 (8)	83 (9)	-56 (8)	2.52
N(4)	21186 (18)	58764 (17)	5630 (17)	529 (14)	445 (13)	357 (13)	238 (11)	72 (11)	-35 (10)	3.44
C(1)	29507 (20)	40743 (18)	6541 (21)	436 (14)	248 (11)	494 (16)	-16 (10)	152 (12)	59 (10)	2.83
C(2)	40989 (19)	53234 (19)	8861 (21)	344 (13)	339 (12)	429 (15)	-50 (10)	57 (11)	-4 (11)	2.79
C(3)	31176 (20)	49929 (17)	-7793 (19)	451 (14)	286 (11)	328 (13)	-52 (10)	133 (11)	-62 (10)	2.60
C(4)	16729 (20)	51220 (23)	-1384 (22)	308 (13)	558 (17)	455 (17)	90 (12)	48 (11)	-46 (14)	3.37
C(5)	28408 (25)	63643 (18)	1051 (22)	733 (20)	227 (11)	410 (16)	95 (12)	53 (14)	-1 (11)	3.46
C(6)	26472 (23)	54461 (22)	15345 (20)	535 (17)	485 (16)	294 (14)	171 (13)	113 (12)	11 (12)	3.31

The initial weights were  $w=1.0$  ( $w=1/\sigma^2$ ). During the last cycles of refinement, the weighting scheme was

$$\begin{aligned} \sigma &= 1.34 \text{ for } |F_o| \leq 6.0 \\ \sigma &= 1.16 \text{ for } 6.0 < |F_o| \leq 43.0 \\ \sigma &= 1.45 \text{ for } |F_o| > 43.0. \end{aligned}$$

The final  $R$  was 0.036 ( $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.042$ ).

Positional and thermal parameters are listed in Tables 2 and 3.

Table 3. Hydrogen-atom parameters ( $\times 10^3$ ) of the HMT molecule

The values of the standard deviations are 0.003 for all the parameters. The isotropic thermal parameters are those of the carbon atoms to which they are bonded.

	$x/a$	$y/b$	$z/c$	$x/a$	$y/b$	$z/c$	
H1(C1)	249	372	99	H2(C1)	350	361	52
H1(C2)	442	581	138	H2(C2)	462	488	78
H1(C3)	362	453	-89	H2(C3)	276	528	-146
H1(C4)	116	474	12	H2(C4)	130	541	-80
H1(C5)	251	668	-54	H2(C5)	322	689	60
H1(C6)	297	597	204	H2(C6)	216	508	184

### Description and discussion of the structure

Fig. 1 shows the structure viewed along  $c$ . All distances and angles, with their e.s.d.'s, were calculated with the NRC programs (Ahmed, Hall, Pippy & Huber, 1966).

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30678 (21 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

In the following description of the structure, we denote by 'i' the atomic positions contained in the asymmetric unit ( $x, y, z$ ) and by 'iii' the equivalent positions ( $-x, y, \frac{1}{2} - z$ ).

### Dichromate ion

Interatomic distances, angles and their e.s.d.'s for the dichromate ion are listed in Table 4.

There is one  $\text{CrO}_4$  group in the asymmetric unit, the fourth oxygen atom being in special position ( $0, y, \frac{1}{4}$ ). The  $\text{Cr}_2\text{O}_7^{2-}$  ion consists of two  $\text{CrO}_4$  groups (one in the 'i' position, the other in the 'iii' position) joined through a shared O(B) on the glide plane.

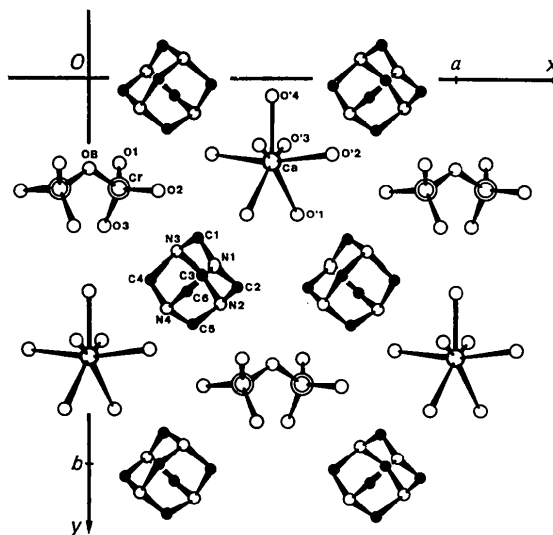


Fig. 1. The structure viewed along  $c$  (molecules related by a centre of symmetry are not shown).

Table 4. *Interatomic distances (Å) and angles (°) for the dichromate ion with e.s.d.'s in parentheses*

Cr <sup>I</sup> —Cr <sup>III</sup>	3.184 (1)	Cr—O(2)	1.590 (2)
Cr—O(B)	1.764 (1)	Cr—O(3)	1.598 (2)
Cr—O(1)	1.598 (2)	Mean Cr—O(terminal)	1.595
O(B)—O(1)	2.711 (3)	O(B)—Cr—O(1)	107.4 (1)
O(B)—O(2)	2.749 (3)	O(B)—Cr—O(2)	110.0 (1)
O(B)—O(3)	2.769 (3)	O(B)—Cr—O(3)	110.8 (1)
Mean O—O(bridge)	2.743	Mean O—Cr—O(bridge)	109.4
O(1)—O(2)	2.599 (4)	O(1)—Cr—O(2)	109.2 (1)
O(1)—O(3)	2.592 (3)	O(1)—Cr—O(3)	108.4 (1)
O(2)—O(3)	2.628 (4)	O(2)—Cr—O(3)	111.1 (1)
Mean O—O(terminal)	2.606	Mean O—Cr—O(terminal)	109.6

The CrO<sub>4</sub> group is a slightly distorted tetrahedron with Cr—O(B) distance (1.764 Å) which is longer than the other three Cr—O distances (mean: 1.595 Å) as is generally the case in X<sub>2</sub>O<sub>7</sub> ions (Brandon & Brown, 1967; Lynton & Truter, 1960). The O—Cr—O angles are not significantly different from 109.5°. The Cr<sup>I</sup>—O(B)—Cr<sup>III</sup> angle is 129.0°.

#### HMT molecule

Bond lengths, angles and their e.s.d.'s for the HMT molecule are shown in Table 5. Their mean values are in good agreement with those found by Becka & Cruickshank (1963) for HMT and with those found in magnesium dichromate HMT hexahydrate (Dahan, 1974).

#### [Ca(H<sub>2</sub>O)<sub>7</sub>]<sup>2+</sup> group

The bond lengths, angles and their e.s.d.'s for the coordination polyhedron around Ca are given in Table 6.

The calcium is a heptahydrated cation and does not coordinate with the dichromate oxygen atoms.

The Ca—O distances range from 2.328 to 2.427 Å. Proceeding on the assumption that any Ca—O distance

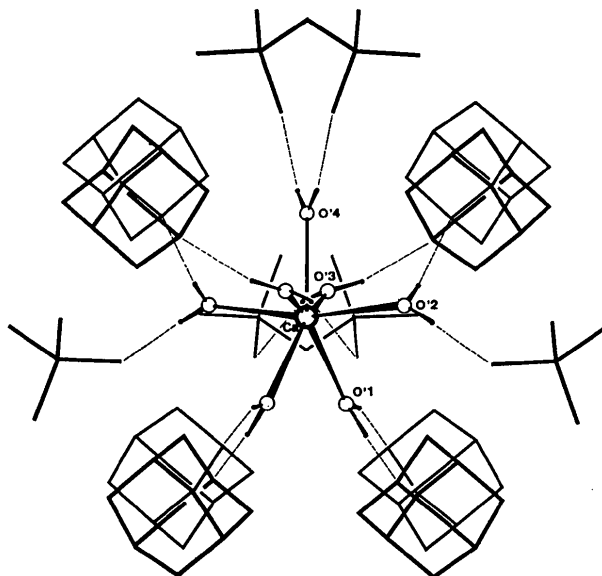


Fig. 2. Environment of the calcium atom.

less than 2.50 Å denotes a strong Ca—O bond, we note that the bonding of the Ca ion to all water oxygen atoms is strong. Within the calcium shell there is a short oxygen—oxygen contact [O'(1)<sup>I</sup>—O'(1)<sup>III</sup> = 2.731 Å], although there are no hydrogen bonds between the water oxygen atoms.

Table 5. *Bond lengths (Å) and angles (°) for the HMT molecule with e.s.d.'s in parentheses*

C(1)—N(1)	1.477 (3)	C(1)—N(3)	1.479 (3)
C(2)—N(1)	1.475 (3)	C(3)—N(3)	1.466 (3)
C(6)—N(1)	1.468 (4)	C(4)—N(3)	1.475 (4)
C(2)—N(2)	1.468 (3)	C(4)—N(4)	1.477 (4)
C(3)—N(2)	1.468 (3)	C(5)—N(4)	1.473 (4)
C(5)—N(2)	1.465 (4)	C(6)—N(4)	1.478 (4)
Mean C—N	1.472		
C(1)—N(1)—C(2)	107.8 (2)	C(1)—N(3)—C(3)	107.9 (2)
C(1)—N(1)—C(6)	108.1 (2)	C(1)—N(3)—C(4)	108.4 (2)
C(2)—N(1)—C(6)	108.6 (2)	C(3)—N(3)—C(4)	107.8 (2)
C(2)—N(2)—C(3)	108.6 (2)	C(4)—N(4)—C(5)	108.6 (2)
C(2)—N(2)—C(5)	107.7 (2)	C(4)—N(4)—C(6)	107.8 (2)
C(3)—N(2)—C(5)	108.2 (2)	C(5)—N(4)—C(6)	108.0 (2)
Mean C—N—C	108.1		
N(1)—C(1)—N(3)	112.0 (2)	N(3)—C(4)—N(4)	111.8 (2)
N(1)—C(2)—N(2)	112.0 (2)	N(2)—C(5)—N(4)	112.2 (2)
N(2)—C(3)—N(3)	112.6 (2)	N(1)—C(6)—N(4)	112.0 (2)
Mean N—C—N	112.1		
C(1)—H1(C1)	1.01 (4)	C(4)—H1(C4)	1.03 (4)
C(1)—H2(C1)	1.06 (4)	C(4)—H2(C4)	1.01 (4)
C(2)—H1(C2)	0.99 (4)	C(5)—H1(C5)	0.99 (4)
C(2)—H2(C2)	1.01 (4)	C(5)—H2(C5)	1.07 (4)
C(3)—H1(C3)	1.00 (4)	C(6)—H1(C6)	1.04 (4)
C(3)—H2(C3)	1.02 (4)	C(6)—H2(C6)	1.02 (4)
Mean C—H	1.02		
H1(C1)—C(1)—H2(C1)	109 (2)	H1(C4)—C(4)—H2(C4)	104 (3)
H1(C2)—C(2)—H2(C2)	108 (2)	H1(C5)—C(5)—H2(C5)	106 (3)
H1(C3)—C(3)—H2(C3)	111 (2)	H1(C6)—C(6)—H2(C6)	110 (3)
Mean H—C—H	108		

Table 6. *Bond lengths (Å) and angles (°) for the coordination polyhedron around Ca with e.s.d.'s in parentheses*

Ca—O'(1)	2.427 (2)	Ca—O'(3)	2.389 (2)
Ca—O'(2)	2.328 (2)	Ca—O'(4)	2.421 (3)
		Mean Ca—O'	2.391
O'(1)—O'(2)	3.062 (3)	O'(1)—Ca—O'(2)	80.14 (7)
O'(1)—O'(3)	2.928 (3)	O'(1)—Ca—O'(3)	74.86 (7)
O'(2)—O'(3)	3.318 (3)	O'(2)—Ca—O'(3)	89.42 (7)
O'(2)—O'(4)	3.152 (3)	O'(2)—Ca—O'(4)	83.16 (6)
O'(3)—O'(4)	2.939 (3)	O'(3)—Ca—O'(4)	75.31 (7)
Mean O'—O'	3.080	Mean O'—Ca—O'	80.58

Table 7. Observed hydrogen-bond parameters compared with those predicted by geometrical calculations (printed below)

X is the water oxygen atom and Y the hydrogen-bond acceptor atom.

	Atomic coordinates			Atom X	X-H(Å)	Atom Y	H...Y(Å)	X...Y(Å)	X-H...Y(°)
	x/a	y/b	z/c						
H1(O'1)	0.089	0.859	0.139	O'1	0.81	N2(vi)	2.24	3.011	160
	0.079	0.861	0.122		0.97		2.11		155
H2(O'1)	0.097	0.901	0.235	O'1	0.94	N1(vii)	2.07	2.989	166
	0.103	0.901	0.235		0.97		2.05		162
H1(O'2)	0.210	0.724	0.302	O'2	0.90	O2(vii)	2.03	2.922	179
	0.218	0.722	0.304		0.97		1.96		172
H2(O'2)	0.189	0.658	0.372	O'2	0.80	N3(iv)	1.99	2.785	172
	0.190	0.645	0.377		0.97		1.82		178
H1(O'3)	0.092	0.654	0.072	O'3	0.90	N4(i)	1.99	2.871	166
	0.096	0.642	0.084		0.97		1.90		173
H2(O'3)	-0.001	0.689	0.039	O'3	0.79	O1(ii)	2.26	3.017	163
	0.007	0.703	0.025		0.97		2.08		163
H(O'4)	0.018	0.510	0.210	O'4	0.82	O3(i)	2.08	2.863	158
	0.020	0.507	0.199		0.97		1.97		152

In crystalline structures of calcium compounds, especially when hydrated, the calcium ion is generally surrounded by eight oxygen atoms (Furberg & Helland, 1962; Bugg & Cook, 1972; Cook & Bugg, 1973; Bugg, 1973; Einspahr & Bugg, 1974). Sometimes, the environment is of seven oxygen atoms (Dickens, Brown, Kruger & Stewart, 1973) as in this study. In comparable structures, where the Ca ion is replaced by Mg, nearly always an octahedral environment occurs (Baur, 1964; Whitaker & Jeffery, 1970; Dahan, 1974).

#### Hydrogen bonding

The hydrogen-bonding system between the  $[\text{Ca}(\text{H}_2\text{O})_7]^{2+}$  polyhedron, the HMT molecules and the dichromate ion is shown in Fig. 2.

The coordinates of the hydrogen atoms of the water molecules, the distances and angles involved in the hydrogen-bonding system as well as those predicted by geometrical calculations (CALHPO: Baur, 1971, 1972) are given in Table 7. The shape of the water molecule is held constant: O-H=0.97 Å and H-O-H=109.5°. The hydrogen atoms of the water molecules are presumed to be in a plane defined by a water oxygen atom and the two hydrogen-bonding acceptor atoms, and as far as possible from the calcium atom.

The comparison between observed and calculated values shows that the observed O-H bonds are shorter than the calculated.

All the nitrogen atoms of the HMT molecules and all the terminal oxygen atoms of the dichromate ion are hydrogen bonded to the water molecules.

The hydrogen-bonding distances O(water)-H...O (dichromate) (mean 2.934 Å) and O(water)-H...N (HMT) (mean 2.914 Å) are in good agreement with the values given by Hamilton & Ibers (1968) in crystalline hydrates.

The structures of the two crystal hydrates,  $\text{Cr}_2\text{O}_7 \cdot X \cdot 2(\text{HMT}) \cdot n\text{H}_2\text{O}$  (X=Mg, Ca, and  $n=6, 7$ ) can be regarded as being composed of slightly distorted  $\text{CrO}_4$  tetrahedra joined through a shared oxygen atom, of a polyhedron around the metal atom and the HMT molecules. There are no coordination bonds between

these groups: the hydrogen bonds link them, thus determining the packing and controlling the stability.

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