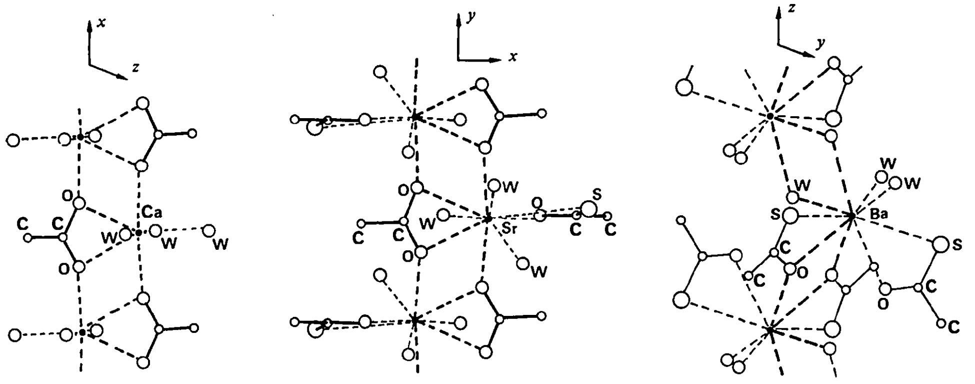

Fig. 2. Environnement du métal et chaînes formées suivant la direction d'allongement des cristaux de $Ca(CH_3COO)(CH_3COS).3H_2O$, $Sr(CH_3COO)(CH_3COS).4H_2O$ et $Ba(CH_3COS)_2.3H_2O$.

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The Crystal Structure of Guanidinium Chromate

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Crystals of $(CN_3H_6)_2CrO_4$ are triclinic, space group $P\bar{1}$, with $a=6\cdot540\ (1)$, $b=6\cdot732\ (1)$, $c=10\cdot660\ (1)$ Å, $\alpha=94\cdot67\ (1)$, $\beta=97\cdot03\ (1)$, $\gamma=97\cdot37\ (1)^\circ$, $Z=2$. 1888 independent reflexions were measured on a single-crystal diffractometer (Cu $K\alpha$ radiation). The structure was solved by the heavy-atom method and refined by full-matrix least squares to the final $R=0\cdot0487$. The configuration of a chromate ion is tetrahedral and guanidinium ions are triangular planar. The ions are linked by a highly specific hydrogen-bond net.

Introduction

Crystals of guanidinium chromate show a marked anisotropy of cohesion forces. They possess a highly perfect cleavage plane (001), an imperfect cleavage plane (100) and undergo plastic deformation very easily. They differ considerably in mechanical properties from guanidinium di- and trichromate crystals (Swaryczewski, 1934). Structures of the last two compounds have been determined (Grabowski, Stępień & Wajsman, 1971; Stępień, 1973; Wajsman, 1975) and a comparison of the properties of all these chromates is in preparation (Grabowski, Cygler, Stępień & Wajsman, 1976).

Experimental

Guanidinium chromate was prepared from guanidinium carbonate by decomposition with chromic acid in water solution (molar ratio 1:1). The crystals obtained by evaporation at room temperature were yellow, prismatic along **b**.

The values of 43 2θ angles were collected on a single-crystal diffractometer. The refinement of the cell parameters was performed by the method of least squares.

Crystal data

Space group $P\overline{1}$
$a = 6{\cdot}540\ (1)$ Å
$b = 6{\cdot}732\ (1)$
$c = 10{\cdot}660\ (1)$
$\alpha = 94{\cdot}67\ (1)^\circ$
$\beta = 97{\cdot}03\ (1)$
$\gamma = 97{\cdot}37\ (1)$
$F(000) = 244$
$Z = 2$
$V = 459{\cdot}700$ Å^3
$D_x = 1{\cdot}706$ g cm^{-3}
$D_m = 1{\cdot}710$
$\mu r(\mathrm{Cu}\ K\alpha) = 1{\cdot}36$.

The crystal used in the X-ray measurements was ground to a sphere 0·25 mm in diameter. The intensities were measured on a four-circle Enraf–Nonius CAD-4 diffractometer by the θ–2θ scan method, up to the limit of $2\theta = 150^\circ$, with Cu $K\alpha$ radiation. 1888 independent reflexions were measured. 305 reflexions with $F_o < 3{\cdot}2$ (in absolute scale) were treated as unobserved. These reflexions were excluded in preliminary calculations but were included in the final calculations. The intensities were corrected for Lp and absorption factors.

Structure determination

To determine which of the two possible space groups $P1$ or $P\overline{1}$ is realized, the $N(z)$ test was performed. The shape of the curve is characteristic of substances with heavy atoms in centrosymmetric positions (Lipson & Cochran, 1966) and no choice of space group could be made. Next, the distribution of the normalized structure factors was investigated. This indicated $P1$ as the more likely group.

The positions of Cr and the four O atoms were determined from the Patterson function. Two cycles of electron density approximation gave the positions of all non-hydrogen atoms. The model obtained was pseudo-centrosymmetric. There was a possibility that it contained fragments of both enantiomers of the 'true' structure. To test this, one of the four guanidinium ions and four O atoms from one chromate ion were assumed as a basis for the partial structure method (Karle, 1968). Four such variants were investigated. In at least one variant all the atoms should belong to one enantiomer. In all trials, however, the initial model was obtained.

The model was refined in group $P1$. Because of pseudo-centrosymmetry the full-matrix refinement failed. The atomic parameters and isotropic temperature factors have been refined by the block-diagonal least-squares method. In spite of the low R value (0·076 without unobserved reflexions), marked differences in equivalent bond lengths were unsatisfactory from the crystallo-chemical point of view. Instead, the refinement in group $P\overline{1}$ led to quite a satisfactory model. Thus the $P\overline{1}$ group was assumed.

Atomic parameters were refined by full-matrix least squares. Three cycles of isotropic refinement excluding unobserved reflexions were made ($R = 0{\cdot}089$). For anisotropic refinement, atoms were divided into two groups because of the computer core capacity, and the parameters of each group were refined alternately. After two cycles of refinement including unobserved reflexions, R dropped to 0·056 (for observed reflexions). At this stage the difference synthesis was calculated. All 12 hydrogen atoms were located among the 14 highest peaks of the map. In subsequent cycles of refinement hydrogen atoms were treated as isotropic; B_{iso} was assumed to be equal to the B_{iso} of the neighbouring N atom and was not refined. The atoms were then divided into three groups and the parameters of each group were refined alternately. Three

Table 1. *Final coordinates and anisotropic thermal parameters β_{ij} ($\times 10^4$) with standard deviations resulting from the least-squares refinement*

The β_{ij} values given are defined by the temperature factor $\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\right]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr(1)	0·22693 (7)	0·23334 (7)	0·23337 (5)	99 (1)	98 (1)	50 (1)	25 (1)	15 (1)	17 (1)
O(1)	0·2362 (4)	0·2455 (4)	0·3884 (2)	248 (7)	200 (6)	61 (2)	33 (5)	40 (3)	19 (3)
O(2)	0·4669 (3)	0·2876 (3)	0·1986 (2)	134 (5)	163 (5)	67 (2)	6 (4)	23 (3)	15 (3)
O(3)	0·1283 (4)	0·0025 (3)	0·1725 (2)	151 (5)	142 (5)	89 (2)	6 (4)	14 (3)	8 (3)
O(4)	0·0851 (4)	0·3969 (4)	0·1782 (3)	205 (6)	187 (6)	103 (3)	95 (5)	10 (3)	37 (3)
C(1)	0·6113 (5)	0·7788 (4)	0·1195 (3)	159 (7)	141 (6)	39 (2)	41 (5)	11 (3)	18 (3)
C(2)	0·2227 (5)	0·7640 (5)	0·5014 (3)	144 (7)	147 (6)	57 (3)	12 (5)	24 (3)	16 (3)
N(1)	0·6875 (5)	0·9690 (4)	0·1124 (3)	132 (6)	145 (6)	79 (3)	13 (5)	13 (3)	16 (3)
N(2)	0·7350 (6)	0·6367 (5)	0·1179 (3)	226 (8)	201 (8)	83 (3)	109 (7)	19 (4)	19 (4)
N(3)	0·4128 (5)	0·7285 (5)	0·1268 (3)	188 (8)	135 (6)	109 (4)	10 (6)	52 (4)	33 (4)
N(4)	0·2573 (5)	0·6024 (5)	0·5603 (3)	211 (8)	168 (7)	68 (3)	18 (6)	−13 (4)	27 (4)
N(5)	0·2701 (6)	0·9465 (5)	0·5634 (3)	292 (10)	159 (7)	66 (3)	−1 (6)	6 (4)	10 (4)
N(6)	0·1329 (5)	0·7427 (5)	0·3823 (3)	286 (9)	169 (7)	53 (2)	35 (6)	12 (4)	15 (3)

Table 1 (*cont.*)

	x	y	z	B
H(1)	0·7951 (93)	0·9940 (80)	0·1110 (51)	2·9
H(2)	0·6142 (88)	0·0541 (86)	0·1143 (51)	2·9
H(3)	0·6762 (91)	0·5213 (95)	0·1277 (54)	3·4
H(4)	0·8531 (95)	0·6624 (85)	0·1101 (53)	3·4
H(5)	0·3291 (92)	0·8216 (89)	0·1324 (54)	3·4
H(6)	0·3651 (92)	0·6252 (93)	0·1428 (56)	3·4
H(7)	0·3180 (90)	0·6148 (83)	0·6268 (58)	3·2
H(8)	0·2324 (89)	0·4818 (92)	0·5135 (53)	3·2
H(9)	0·2528 (92)	0·0434 (92)	0·5120 (56)	3·5
H(10)	0·3262 (90)	0·9509 (85)	0·6326 (60)	3·5
H(11)	0·1079 (91)	0·8533 (87)	0·3389 (55)	3·4
H(12)	0·1055 (90)	0·6322 (93)	0·3401 (55)	3·4

cycles of refinement were carried out. The largest shift/e.s.d. in the final cycle was 0·41 and the average shift/e.s.d. was 0·07. In the refinement Cruickshank's weighting scheme, $w^{-1}=A+BF_o+CF_o^2$, was used with A,B,C calculated after each cycle by Lee's (1974) method. Reflexions with $w^{1/2}(F_o-F_c)>1{\cdot}6$ were excluded from the refinement. The extinction correction was not applied but 21 reflexions with high F_o and low θ angles, which were in very bad agreement with F_c, were excluded from refinement and from the final R values. The final agreement indices were: for 1867 reflexions $R=0{\cdot}0487$, $R_w=0{\cdot}0558$; for 1564 'observed' reflexions $R=0{\cdot}0393$, $R_w=0{\cdot}0502$.

Scattering factors for neutral Cr, O, N and C atoms were taken from Cromer & Mann (1968) and those for H from *International Tables for X-ray Crystallography* (1962). The correction for the real part of the anomalous scattering for the Cr atom was made (*International Tables for X-ray Crystallography*, 1962).

NRC Crystallographic Programs (Ahmed, Hall, Pippy & Huber, 1966) were used in all computations except full-matrix refinement where *ORFLS* (Busing, Martin & Levy, 1962) was applied.

Table 1 gives the final atomic parameters with the

Table 2. *Distances* (Å) *and angles* (°) *with estimated standard deviations*

	Uncorrected	Corrected		Uncorrected	Corrected		Uncorrected	Corrected
Cr(1)–O(1)	1·641 (3)	1·658 (3)	C(1)–N(1)	1·325 (4)	1·333 (4)	C(2)—N(4)	1·330 (4)	1·341 (5)
Cr(1)–O(2)	1·659 (2)	1·667 (2)	C(1)–N(2)	1·330 (5)	1·349 (5)	C(2)—N(5)	1·328 (5)	1·343 (5)
Cr(1)–O(3)	1·652 (2)	1·664 (2)	C(1)–N(3)	1·312 (5)	1·329 (5)	C(2)—N(6)	1·320 (4)	1·334 (5)
Cr(1)–O(4)	1·629 (3)	1·648 (3)						
O(1) –O(2)	2·679 (3)		N(1)–H(1)	0·71 (6)		N(4)—H(7)	0·76 (6)	
O(1) –O(3)	2·676 (3)		N(1)–H(2)	0·79 (6)		N(4)—H(8)	0·90 (6)	
O(1) –O(4)	2·669 (3)		N(2)–H(3)	0·84 (6)		N(5)—H(9)	0·90 (6)	
O(2) –O(3)	2·709 (2)		N(2)–H(4)	0·79 (6)		N(5)—H(10)	0·78 (6)	
O(2) –O(4)	2·681 (3)		N(3)–H(5)	0·89 (6)		N(6)—H(11)	0·93 (6)	
O(3) –O(4)	2·702 (3)		N(3)–H(6)	0·77 (6)		N(6)—H(12)	0·82 (6)	
O(1) –Cr(1)–O(2)		108·6 (1)	N(1)–C(1) —N(2)		120·3 (3)	N(4)—C(2)——N(5)		120·2 (3)
O(1) –Cr(1)–O(3)		108·7 (1)	N(1)–C(1)—N(3)		120·3 (3)	N(4)—C(2)——N(6)		120·0 (3)
O(1) –Cr(1)–O(4)		109·4 (1)	N(2)–C(1)—N(3)		119·4 (3)	N(5)—C(2)——N(6)		119·7 (3)
O(2) –Cr(1)–O(3)		109·8 (1)	H(1)–N(1)—H(2)		120 (6)	H(7)—N(4)——H(8)		121 (6)
O(2) –Cr(1)–O(4)		109·3 (1)	H(3)–N(2)—H(4)		125 (6)	H(9)—N(5)——H(10)		131 (6)
O(3) –Cr(1)–O(4)		110·9 (1)	H(5)–N(3)—H(6)		113 (6)	H(11)–N(6)——H(12)		116 (6)

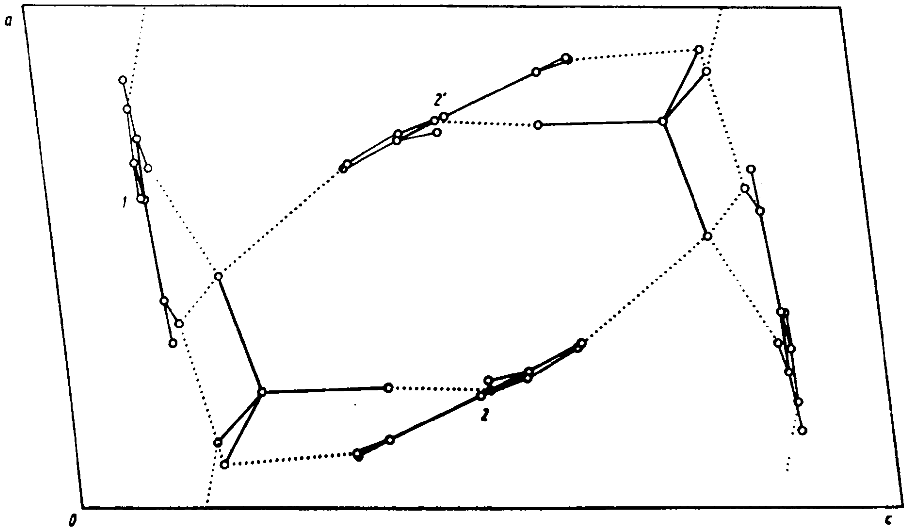

Fig. 1. The projection of the structure down the y axis. Hydrogen bonds are marked by dotted lines.

e.s.d.'s. Bond distances and angles are listed in Table 2.* All interatomic distances within the chromate and the guanidinium ions were corrected for librational thermal motion with the program *ORFFE*3 (Busing, Martin & Levy, 1971).

Discussion

The chromate ion forms a nearly regular tetrahedron with a mean (corrected) Cr–O bond distance of 1·659 Å. This value is in agreement with those obtained for other chromates (*e.g.* Stephens & Cruickshank, 1970). The maximum difference in O–O distances is 0·04 Å. This value is of the same order as that obtained in $NaNH_4CrO_4.2H_2O$ (0·03 Å) (Khan & Baur, 1972) and in $(NH_4)_2CrO_4$ (0·04 Å) (Stephens & Cruickshank, 1970). The deformation of the chromate tetrahedron in $(CN_3H_6)_2CrO_4$ is probably related to a highly specific hydrogen-bond system. The dependence of Cr–O distance upon the number and strength of hydrogen bonds formed by different O atoms has been found in that structure (Table 3). Because of the large size of the guanidinium ions, the effect of electrostatic crystal forces upon the deformation of the chromate tetrahedron seems to be rather small, contrary to K_2CrO_4 (McGinnety, 1972) and $Na_2CrO_4.4H_2O$ (Ruben, Olovsson, Zalkin & Templeton, 1973), where this effect is mainly responsible for deformation.

Table 3. *The number and strength of hydrogen bonds formed by different oxygen atoms*

Atom	Number of bonds	Mean N···O distance (Å)	Cr–O distance (Å)
O(2)	4	2·998	1·667
O(3)	3	2·880	1·664
O(1)	2	2·872	1·658
O(4)	2	3·018	1·648

Both of the guanidinium ions in the asymmetric unit are triangular planar. The variations in the bond distances and angles for the ions are less than two standard deviations. The mean C–N distance is 1·339 Å (thermally corrected) and the mean N–H distance is 0·82 Å. These are in agreement with previous guanidinium data (Haas, Harris & Mills, 1965). The maximum distance of the non-hydrogen atoms from the 'best' planes obtained by the least-squares method is 0·015 Å. Only one atom, H(6), deviates from the plane by more then 0·1 Å. This atom forms a bifurcated hydrogen bond considerably inclined to the ion plane. The equations of the best planes and the distances of the atoms from these planes are given in Table 4.

The projections of the structure down the *y* and *z* axes are shown in Figs. 1 and 2 respectively.

Table 4. *Deviations of atoms from the least-squares planes*

Plane equations

Guanidinium ion 1

$$0\cdot3172x+0\cdot2653y+12\cdot4137z-1\cdot8796=0$$

Guanidinium ion 2

$$6\cdot3568x-0\cdot1940y-4\cdot5978z+1\cdot0523=0$$

Deviations (Å)

C(1)	0·005	C(2)	−0·015
N(1)	−0·009	N(4)	0·005
N(2)	−0·013	N(5)	0·005
N(3)	0·017	N(6)	0·005
H(1)	0·015	H(7)	−0·073
H(2)	0·002	H(8)	−0·075
H(3)	0·059	H(9)	−0·103
H(4)	−0·066	H(10)	−0·033
H(5)	0·087	H(11)	−0·015
H(6)	0·175	H(12)	−0·037

Table 5. *Hydrogen bonds*

	N···O (Å)	H···O (Å)	∠N–H···O (°)
N(1) $O(2^{i})$	2·885 (4)	2·14 (6)	156 (6)
N(1) $O(3^{ii})$	2·851 (4)	2·19 (6)	157 (6)
N(2) O(2)	2·996 (4)	2·19 (6)	159 (6)
N(3) $O(3^{i})$	2·839 (4)	1·96 (6)	169 (6)
N(3) O(4)	3·023 (4)	2·32 (6)	152 (6)
N(3) O(2)	3·177 (5)	2·55 (6)	141 (6)
N(4) O(1)	2·879 (4)	2·00 (6)	166 (5)
N(4) $O(2^{iii})$	2·936 (6)	2·19 (6)	166 (6)
N(5) $O(1^{i})$	2·865 (4)	1·97 (6)	174 (6)
N(6) $O(3^{i})$	2·949 (4)	2·12 (6)	148 (6)
N(6) O(4)	3·012 (4)	2·23 (6)	160 (6)

Symmetry code

Superscript			
i	x	$1+y$	z
ii	$1+x$	$1+y$	z
iii	$1-x$	$1-y$	$1-z$

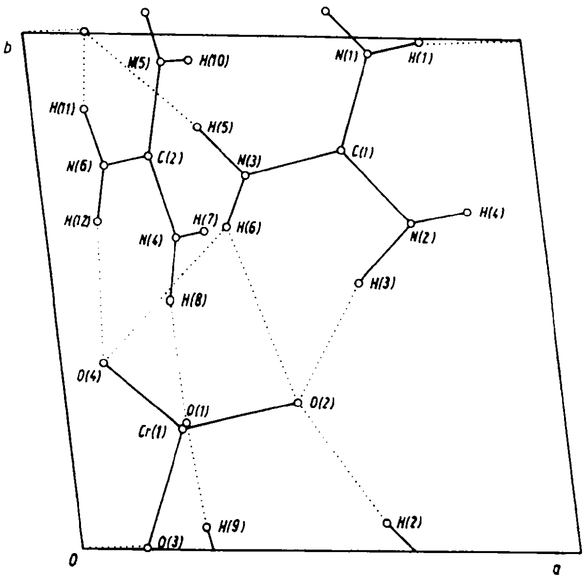

Fig. 2. The projection of the structure down the *z* axis. Hydrogen bonds are marked by dotted lines.

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* A list of structure factors has been deposited with The British Library Lending Division as Supplementary Publication No. SUP 31689 (17 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The list of atoms with N···O distances less than 3·3 Å and N–H–O angles more than 140° is given in Table 5. Of the twelve hydrogen atoms, ten take part in hydrogen bonding. One of these, H(6), forms a bifurcated hydrogen bond.

The whole hydrogen-bonding system enables chains, layers and double-layers of ions to be identified according to the strength and number of bonds. The chains elongated in the *y* direction are built from chromate and guanidinium ions. The neighbouring chromate ions are joined by numerous hydrogen bonds through three guanidinium ions (1, 2, 2′ in Fig. 1). The chains are connected by hydrogen bonds through guanidinium ion 1 in the *x* direction. They form layers parallel to (001). These layers are joined in pairs by hydrogen bonds through guanidinium ion 2, in this way forming double-layers. There are no hydrogen bonds between neighbouring double-layers. The shortest distance between atoms of the different double-layers is 3·30 Å. This value indicates that the double-layers are connected by van der Waals forces.

The guanidinium ions are characteristically oriented in the structure. Ion 1 is oriented along the layers while ion 2 is nearly perpendicular to them.

The double-layer structure found in these crystals explains the perfect cleavage along (001). The imperfect cleavage (100) also has a structural explanation. The ions are distributed on both sides of the (100) plane (Fig. 1). These two groups of ions are connected by a small number of hydrogen bonds and van der Waals bonds.

The consistences of the mechanical properties of crystals with the hydrogen-bond net suggests that the electrostatic forces are of minor importance in the formation of the crystal structure of this compound.

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