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Guanidinium Trichromate

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Abstract. $(CN_3H_6)_2Cr_3O_{10}$, monoclinic, space group $C2/c$, with $a = 13{\cdot}303\,(4)$, $b = 7{\cdot}791\,(2)$, $c = 14{\cdot}667\,(4)$ Å, $\beta = 107{\cdot}08\,(3)°$, $V = 1510{\cdot}75$ Å^3, $Z = 4$, $D_m = 1{\cdot}998$, $D_x = 2{\cdot}00$ g cm^{-3}. 618 independent non-zero reflexions were estimated by photographic methods; systematic absences: hkl, $h + k = 2n + 1$, $h0l$, $l = 2n + 1$. The structure was solved by the Patterson method and refined by full-matrix least squares; the final R is 0·135. The trichromate ion consists of three nearly tetrahedral CrO_4 groups joined through shared O atoms. The value of the Cr–O–Cr angle is 132·7°. The mean (uncorrected) Cr–O bond distances are 1·75 Å and 1·65 Å for bridge and terminal bonds respectively. The ions are linked by N–H···O hydrogen bonds.

Introduction. Cr, like S, P, As and some other elements, exhibits a tendency to form polyions. Of these, the following are structurally well known: chromates and dichromates of alkaline metals (Martin & Durif, 1964; McGinnety, 1972; Carter & Margulis, 1972; Panagiotopoulos & Brown, 1970, 1972*a*,*b*, 1973; Brandon & Brown, 1968; Panagiotopoulos, 1972; Löfgren, 1971; Löfgren & Waltersson, 1971), ammonium (Stephens & Cruickshank, 1970; Byström & Wilhelmi, 1951) and guanidinium (Cygler, Grabowski, Stępień & Wajsman, 1976; Wajsman, Cygler, Grabowski & Stępień, 1976).

The trichromate ion has been studied once by X-ray diffraction so far – in rubidium trichromate (Löfgren, 1974). It seemed interesting to determine the structure of the trichromate ion joined to cations not only through ionic bonds, but also hydrogen bonds. On the other hand, crystals of guanidinium chromate, dichromate and trichromate display great differences in mechanical properties. The guanidinium chromate crystals possess cleavage planes and undergo plastic deformation very easily. The crystals of guanidinium dichromate are hard and those of guanidinium trichromate are brittle but possess no cleavage planes and are not plastic. To elucidate the problem of the structure dependence of the above mentioned properties, the crystal structure investigations of the chromate (Cygler, Grabowski, Stępień & Wajsman, 1976) and the dichromate (Wajsman, Cygler, Grabowski & Stępień, 1976) were undertaken. The present paper is a continuation of an earlier investigation of the guanidinium trichromate crystal structure (Stępień, 1973).

Crystals chosen for X-ray analysis were ground into a cylindrical shape ($\mu r = 1{\cdot}5$). The accurate cell constants were obtained by least-squares methods from Weissenberg photographs. The diffraction data were collected from the integrated Weissenberg photographs taken with Cu $K\alpha$ radiation. The intensities were corrected for Lp and absorption factors for a cylinder (*International Tables for X-ray Crystallography*, 1962).

The structure was determined by the heavy-atom method, with a three-dimensional Patterson synthesis. From the analysis of this function two Cr atoms were located, one of which must have been in a special position on the twofold axis. Five O atoms were also located. The positions of the remaining non-hydrogen atoms were located with the electron density function. The structure was refined by the full-matrix least-squares method, taking into account the Cruickshank weighting scheme, $w^{-1} = A + BF_o + CF_o^2$, with A, B, and C calculated after each cycle by Lee's (1974) method. The first three cycles were carried out with isotropic temperature factors and the last four with anisotropic factors. H atoms were located by difference syntheses and $w^2 - \beta$ syntheses (Ramachandran, 1964). The progress of the refinement is shown in Table 1.

The final positional parameters are listed in Table 2, along with their standard deviations.[*] The interatomic distances and bond angles are given in Table 3; the values have not been corrected for thermal motion. The atomic factors were taken from *International Tables for X-ray Crystallography* (1962).

Discussion. The trichromate ion consists of three tetrahedral CrO_4 groups joined at the corners through shared O atoms. The bonding of the central tetrahedron, both in the ion and in the crystal, is different from that of the terminal tetrahedra. From this difference arise the differences in the structures of central and terminal tetrahedra.

The central Cr atom lies in a special position – on the twofold axis. That is why in the trichromate ion only half the ion is symmetrically independent: the terminal and half the central tetrahedron.

Table 1. *Progress of refinement*

	R
Heavy atoms from three-dimensional Patterson function	0·285
All atoms from the electron density function	0·254
Three cycles of least squares with isotropic temperature factors	0·166
Four cycles with anisotropic temperature factors	0·135

Table 2. *Fractional coordinates with standard deviations resulting from the least-squares refinement*

	x	y	z
Cr(1)	0·1457 (3)	0·1883 (6)	0·1830 (3)
Cr(2)	0	−0·0821 (6)	0·25
O(1)	0·1008 (14)	0·0616 (23)	0·2650 (12)
O(2)	0·0936 (14)	0·1107 (21)	0·0750 (15)
O(3)	0·2776 (18)	0·1958 (26)	0·2163 (14)
O(4)	0·0968 (17)	0·3815 (28)	0·1861 (17)
O(5)	−0·0106 (14)	−0·1981 (24)	0·1524 (17)
C(1)	0·1671 (16)	0·5507 (27)	−0·0079 (18)
N(1)	0·1209 (20)	0·6445 (32)	0·0451 (19)
N(2)	0·2546 (17)	0·4706 (23)	0·0389 (18)
N(3)	0·1207 (14)	0·5360 (22)	−0·1017 (17)

Table 3. *Intraionic distances* (Å) *and angles* (°) *with estimated standard deviations*

The superscript indicates the position: (i) $-x, y, \frac{1}{2}-z$.

Cr(1)–O(1)	1·80 (2)	Cr(2)–O(5)	1·66 (2)
Cr(1)–O(2)	1·64 (2)	C(1)–N(1)	1·34 (2)
Cr(1)–O(3)	1·67 (2)	C(1)–N(2)	1·31 (2)
Cr(1)–O(4)	1·65 (2)	C(1)–N(3)	1·33 (2)
Cr(2)–O(1)	1·71 (2)		

Mean Cr–O distance	1·69
Mean Cr–O bridging distance	1·75
Mean Cr–O terminal distance	1·65
Mean C–N distance	1·33

O(1)–Cr(1)–O(2)	108·6 (9)	O(1)–Cr(2)–O(5)	109·2 (10)
O(1)–Cr(1)–O(3)	111·0 (10)	O(1)–Cr(2)–O(5^{i})	112·4 (11)
O(1)–Cr(1)–O(4)	105·5 (10)	O(1)–Cr(2)–O(1^{i})	98·3 (10)
O(2)–Cr(1)–O(3)	113·0 (10)	O(5)–Cr(2)–O(5^{i})	114·3 (11)
O(2)–Cr(1)–O(4)	108·1 (11)		
O(3)–Cr(1)–O(4)	110·4 (11)	Cr(1)–O(1)–Cr(2)	132·7 (11)
N(1)–C(1)–N(2)	116·4 (23)		
N(1)–C(1)–N(3)	119·7 (23)		
N(2)–C(1)–N(3)	123·8 (22)		

In the terminal tetrahedron there are three terminal bonds and one bridging bond. The mean value of the lengths of terminal bonds in this tetrahedron is 1·65 Å, while the bridging-bond distance is 1·80 Å. In the central tetrahedron the terminal-bond distance is 1·66 Å and the bridging-bond distance is 1·71 Å. The mean value of terminal bonds for the whole trichromate ion is 1·65 Å while that of bridging bonds is 1·75 Å. These distances show that bridging bonds are strongly differentiated, depending on the location in central or terminal tetrahedra. The distances are very close to those obtained by Löfgren (1974) for $Rb_2Cr_3O_{10}$ (1·81 and 1·71 Å). Löfgren discusses the dependence of bridging-bond distance differences on the number of connected tetrahedra.

The mean value of terminal bonds in guanidinium trichromate (1·65 Å) is much greater than the values of analogous bonds in rubidium trichromate (1·59 Å). The difference may be explained by the differences in interionic forces in both compounds. In $Rb_2Cr_3O_{10}$ we find typical ionic forces, while in $(N_3H_6)_2Cr_3O_{10}$ the guanidinium ion is joined to the trichromate ion through strong hydrogen bonding, which weakens the terminal Cr–O bond, and consequently causes its elongation. The discussed differences in interatomic distances may be observed for the terminal Cr–O bond distances in alkaline chromates and dichromates as compared with analogous bond distances in guanidinium chromate and dichromate.

The angle Cr–O–Cr equals 132·7°, which is in good agreement with the values of these angles in polychromates (123–147°). The guanidinium ion is, within the error limit, planar. The equation of the best plane

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[*] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32707 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Distances* (Å) *and angles* (°) *of the interionic contacts*

The superscripts indicate the positions: (i) $x, 1+y, z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (iv) $-x, -y, -z$; (v) $x, 1-y, z-\frac{1}{2}$.

N(1)–O(4)	3·00 (3)	O(4)–H(11)	2·58	N(1)–H(11)–O(4)	107·5
		O(4)–H(12)	3·70	N(1)–H(12)–O(4)	30·6
N(1)–O(5^{i})	2·95 (3)	O(5^{i})–H(11)	2·70	N(1)–H(11)–O(5^{i})	97·8
		O(5^{i})–H(12)	2·63	N(1)–H(12)–O(5^{i})	102·7
N(2)–O(1^{ii})	3·01 (3)	O(1^{ii})–H(21)	3·47	N(2)–H(21)–O(1^{ii})	53·1
		O(1^{ii})–H(22)	2·21	N(2)–H(22)–O(1^{ii})	159·3
N(2)–O(2^{iii})	3·06 (3)	O(2^{iii})–H(21)	2·27	N(2)–H(21)–O(2^{iii})	141·1
		O(2^{iii})–H(22)	3·48	N(2)–H(22)–O(2^{iii})	105·9
N(3)–O(3^{iii})	3·05 (3)	O(3^{iii})–H(31)	3·53	N(3)–H(31)–O(3^{iii})	109·4
		O(3^{iii})–H(32)	2·19	N(3)–H(32)–O(3^{iii})	173·1
N(3)–O(5^{iv})	2·99 (2)	O(5^{iv})–H(31)	3·12	N(3)–H(31)–O(5^{iv})	74·2
		O(5^{iv})–H(32)	2·82	N(3)–H(32)–O(5^{iv})	93·9
N(3)–O(4^{iv})	2·85 (3)	O(4^{iv})–H(31)	2·06	N(3)–H(31)–O(4^{iv})	155·3
		O(4^{iv})–H(32)	3·34	N(3)–H(32)–O(4^{iv})	49·5
N(3)–O(4^{v})	3·10 (3)	O(4^{v})–H(31)	2·84	N(3)–H(31)–O(4^{v})	99·7
		O(4^{v})–H(32)	2·74	N(3)–H(32)–O(4^{v})	107·1

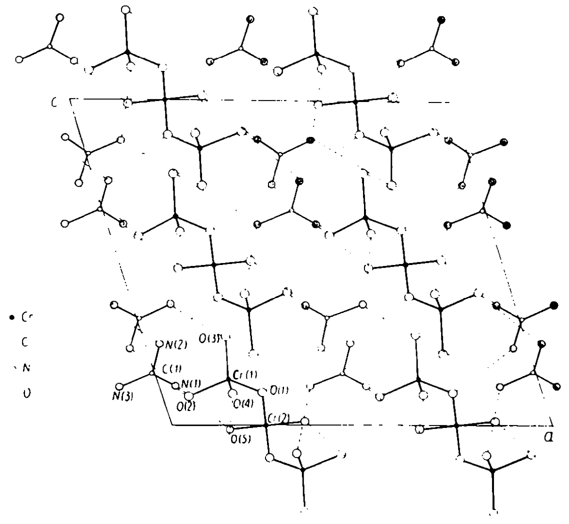

Fig. 1. Projection of the structure down **y**. Hydrogen bonds are marked by dotted lines.

calculated by the least-squares method is: $0{\cdot}6764x + 0{\cdot}7364y - 0{\cdot}2890z - 4{\cdot}6223 = 0$, where x,y,z are coordinates in Å. The deviations of C and N atoms from this plane do not exceed 0·02 Å. The mean value of the C–N bond distance is 1·33 Å, which is identical with the values obtained for guanidinium chromate and dichromate, but somewhat elongated as compared with guanidine.

A projection of the structure down **z** is shown in Fig. 1. There are eight N–O pairs where the interatomic distances within a pair are between 2·85 and 3·10 Å (Table 3). The atoms of these pairs may be linked through hydrogen bonds. In order to specify these bonds, attempts to calculate the positions of the H atoms were made. The difference syntheses gave no result. Approximate parameters of the H atoms were calculated theoretically on the basis of the known geometry of the guanidinium ion. The distances of the O and N from the H atoms, and the N–H···O angles are given in Table 4. From the analysis of these values it appears that N(2) and N(3) are each joined to two O atoms through hydrogen bonds. N(1) is joined to one O through two non-linear hydrogen bonds. Thus, all six H atoms take part in hydrogen-bond formation. Elongations of Cr–O terminal bonds in the trichromate ion and the C–N bonds in the guanidinium ion are due to the above hydrogen bonding.

The three-dimensional net of hydrogen bonds is responsible for the physical properties of the crystals.

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Dendrosterone, a Stigmastane-Type Steroid

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Abstract. $C_{29}H_{44}O_5$, monoclinic, $P2_1$, $a = 17 \cdot 551$ (2), $b = 7 \cdot 280$ (1), $c = 10 \cdot 654$ (3) Å, $\beta = 104 \cdot 64$ (1)°, $Z = 2$, $V = 1317 \cdot 4$ Å^3, $\rho_c = 1 \cdot 19$ g cm^{-3}. Dendrosterone has been isolated as a glucoside from *Dendrobium ochreatum* Lindl. The X-ray determination proved that dendrosterone has a steroid skeleton.

Introduction. Dendrosterone has been isolated as a glucoside from *Dendrobium ochreatum* Lindl. (Behr, Berg, Karlsson, Leander, Pilotti & Wiehager, 1975). Detailed spectroscopic studies and chemical degradation of dendrosterone indicated that it must have either a steroid or a triterpene skeleton, but all attempts to determine a complete structure were unsuccessful. An X-ray analysis of dendrosterone was therefore undertaken. Three-dimensional data were collected from a crystal of approximate volume 0·002 mm^3; a Philips PW 1100 diffractometer, graphite-monochromated Cu $K\alpha$ radiation, and a θ–2θ scan procedure were used. Intensities were measured for all independent reflexions with $2\theta \leq 140°$. Of these, 1697 reflexions had $I_{\text{net}} \geq 3\sigma(I_{\text{net}})$ and were used in the structure refinement. The usual Lorentz and polarization corrections were applied to the data. Lattice constants were obtained from least-squares refinement of the 2θ angles for 25 reflexions.

The structure has been solved with the multisolution program *MULTAN* of Germain, Main & Woolfson (1971). A number of *E* maps gave probable partial structures (the *A*, *B* and *C* ring system, see Fig. 2) located in different parts of the unit cell. Phases from one of these partial structures could be used as a basic set for further refinements. The structure was refined by a least-squares procedure with the weighting scheme of Hughes (1941). Except for the H atom bonded to O(21), which could not be located, the positions of the H atoms were partly deduced from a difference synthesis and partly estimated from chemical considerations. The H positional and thermal parameters

Table 1. *Positional parameters* (×10^4) *of the non-hydrogen atoms with e.s.d.'s in parentheses*

	x	y	z
C(1)	6260 (3)	10816 (10)	3526 (6)
C(2)	7110 (3)	10991 (11)	3429 (6)
C(3)	7558 (3)	9196 (11)	3761 (5)
C(4)	7162 (3)	7670 (11)	2902 (6)
C(5)	6308 (3)	7445 (9)	2986 (5)
C(6)	5872 (3)	5885 (10)	2200 (6)
C(7)	5064 (3)	5519 (10)	2384 (6)
C(8)	4560 (3)	7273	2204 (5)
C(9)	5012 (3)	8852 (9)	3028 (5)
C(10)	5806 (3)	9244 (10)	2683 (5)
C(11)	4500 (3)	10563 (10)	3028 (7)
C(12)	3715 (3)	10114 (10)	3365 (6)
C(13)	3254 (3)	8640 (10)	2461 (5)
C(14)	3787 (3)	6938 (10)	2603 (5)
C(15)	3234 (4)	5417 (11)	1912 (7)
C(16)	2446 (4)	5857 (10)	2244 (6)
C(17)	2548 (3)	7805 (10)	2900 (5)
C(18)	2975 (3)	9372 (12)	1081 (6)
C(19)	5675 (3)	9768 (11)	1250 (5)
O(20)	8358 (2)	9359 (10)	3695 (5)
O(21)	6152 (3)	4967 (10)	1481 (5)
C(22)	1760 (3)	8835 (10)	2613 (5)
C(23)	1810 (4)	10686 (11)	3329 (8)
C(24)	1140 (3)	7700 (10)	3021 (5)
O(25)	1274 (2)	7009 (9)	4090 (4)
C(26)	358 (3)	7529 (10)	2055 (5)
C(27)	−265 (3)	6486 (10)	2532 (5)
C(28)	−64 (3)	4426 (10)	2744 (5)
C(29)	−460 (4)	3576 (11)	1484 (5)
O(30)	−1007 (2)	4695 (9)	784 (4)
C(31)	−1067 (3)	6386 (10)	1532 (5)
C(32)	−353 (5)	3543 (12)	3828 (6)
O(33)	−348 (3)	2062 (9)	1093 (5)
C(34)	−1296 (4)	7952 (11)	620 (7)