

## 1,4-Diazabicyclo[2.2.2]octane-1,4-dium trichromate

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The title compound, (C<sub>6</sub>H<sub>14</sub>N<sub>2</sub>)[Cr<sub>3</sub>O<sub>10</sub>], consists of a diazabicyclo[2.2.2]octane-1,4-dium cation and a discrete trichromate anion linked by an N—H···O hydrogen bond. Three CrO<sub>4</sub> tetrahedra are joined *via* shared O atoms to form the trichromate anion. Supramolecular rings, which can be described by the graph-set motif  $R_4^+(26)$ , are built *via* N—H···O hydrogen bonds, and C—H···O interactions play lesser roles in forming the structure.

## Comment

Many structures of chromates and dichromates have been reported, as well as a few cases of trichromates and sporadic cases of tetrachromates and polychromates (Pressprich *et al.*, 1988). It is almost impossible to predict the real form of these chromium compounds prior to experimental investigation. We report here the synthesis and structure determination of the title salt, (I), and compare its structure with that of other trichromates.

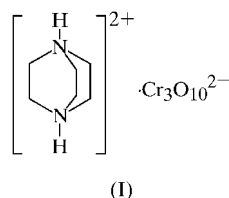


Fig. 1 shows the asymmetric unit of (I), consisting of a diazabicyclo[2.2.2]octane-1,4-dium (DABCO-dium) cation and a discrete trichromate anion that are linked by an N1—H1···O10 hydrogen bond (Table 2). The trichromate anion is composed of three CrO<sub>4</sub> tetrahedra, joined *via* shared O atoms. The Cr—O<sub>t</sub> (terminal O atom) bond lengths are shorter than the Cr—O<sub>b</sub> (bridging O atom) bonds, the mean lengths being 1.599 (5) and 1.77 (3) Å, respectively, with a strong dispersion around these mean values: the Cr—O<sub>t</sub> distances range from 1.581 (2) to 1.618 (2) Å, and the Cr—O<sub>b</sub>

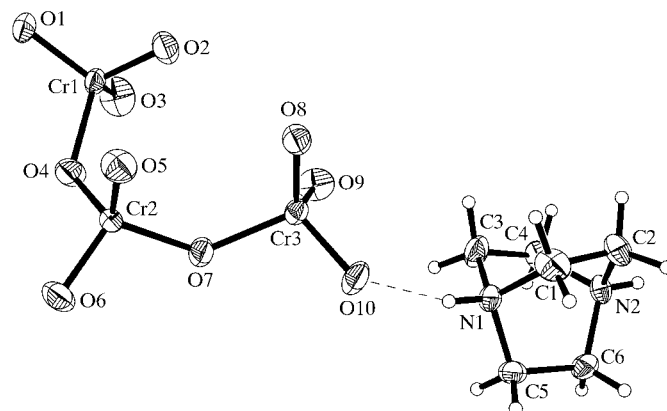


Figure 1

The structure of (I), showing 40% probability displacement ellipsoids and the atom-numbering scheme. The intramolecular hydrogen bond is indicated by a dashed line.

distances range from 1.702 (2) to 1.837 (2) Å (Table 1). The O—Cr—O angles range from 106.17 (13) to 111.71 (12)°, and thus deviate from the ideal value (109.5°). The Cr—O range of the inner Cr2 tetrahedron is comparable to those of the terminal tetrahedra. As indicated by the obvious differences between the magnitudes of the Cr—O<sub>b</sub> and Cr—O<sub>t</sub> distances, as well the great disparity between the values of the O—Cr—O angles, the coordination geometries formed by the four O atoms around the Cr atom are distorted tetrahedra. These results are in good agreement with those reported for Rb<sub>2</sub>Cr<sub>3</sub>O<sub>10</sub> (Blum, 1979*a*), (NH<sub>4</sub>)<sub>2</sub>Cr<sub>3</sub>O<sub>10</sub> (Blum, 1979*b*; Blum & Guitel, 1980), K<sub>2</sub>Cr<sub>3</sub>O<sub>10</sub> (Blum *et al.*, 1979), dipyrazinium trichromate (Pressprich *et al.*, 1988), tetramethylammonium trichromate (Fossé *et al.*, 2001) and α-Cs<sub>2</sub>Cr<sub>3</sub>O<sub>10</sub> (Kolitsch, 2003). The title compound exhibits dissimilar Cr—O—Cr angles [127.34 (12) and 132.80 (12)°; Table 1] and thus differs from guanidinium trichromates [132.7 (11); Stępień & Grabowski, 1977], α-Cs<sub>2</sub>Cr<sub>3</sub>O<sub>10</sub> [136.58 (11) and 140.30 (12)°; Kolitsch, 2003], Rb<sub>2</sub>Cr<sub>3</sub>O<sub>10</sub> [136.0 (4) and 140.0 (4)°; Löfgren, 1974] and dipyrazinium trichromate [137.3 (1) and 137.5 (2)°; Pressprich *et al.*, 1988].

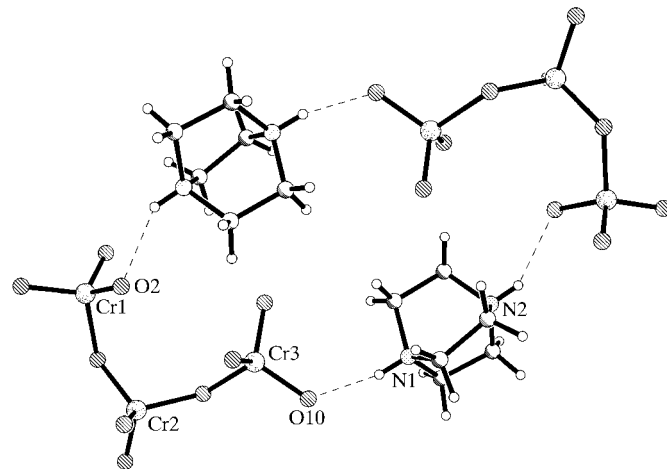


Figure 2

The supramolecular  $R_4^+(26)$  rings of (I), formed *via* N—H···O hydrogen bonds, which are indicated by dashed lines.

In (I), supramolecular rings, which can be described in graph-set notation as  $R_4^4(26)$  (Etter, 1990), are formed *via* N1—H1···O10 and N2—H2···O2(1 -  $x$ , - $y$ , 1 -  $z$ ) hydrogen bonds (Fig. 2). In addition, the rings are stabilized by a number of C—H···O interactions, thus establishing a network structure.

The DABCO-dium ion is distorted, as indicated by the N—C—N torsion angles [mean 13.3 (3) Å]. DABCO has been observed to be disordered across the N···N axis in several cases, including DABCO–biphenol (1:1; Ferguson *et al.*, 1998), DABCO–perchlorate acid (1:1; Katrusiak, 2000) and DABCO–maleic acid (1:2; Sun & Jin, 2002). In (I), DABCO is ordered, owing to the confinement of the C—H···O interactions.

## Experimental

CrO<sub>3</sub> (0.3 mol) and DABCO (0.1 mol) were dissolved separately in water (1.2 and 0.9 mol) and the two solutions were then mixed with cautious stirring. Crystals of the title salt were formed in the final solution by slow evaporation of water at 293 K over a period of one week.

### Crystal data

(C <sub>6</sub> H <sub>14</sub> N <sub>2</sub> )[Cr <sub>3</sub> O <sub>10</sub> ]	$Z = 2$
$M_r = 430.19$	$D_x = 2.073 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.4895$ (6) Å	Cell parameters from 346 reflections
$b = 9.7648$ (8) Å	$\theta = 2.4\text{--}23.0^\circ$
$c = 10.1427$ (8) Å	$\mu = 2.37 \text{ mm}^{-1}$
$\alpha = 87.661$ (1)°	$T = 273$ (2) K
$\beta = 69.497$ (1)°	Block, colorless
$\gamma = 82.771$ (1)°	$0.59 \times 0.58 \times 0.52 \text{ mm}$
$V = 689.26$ (10) Å <sup>3</sup>	

### Data collection

Bruker SMART CCD area-detector diffractometer	2459 independent reflections
$\varphi$ and $\omega$ scans	2336 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2000)	$R_{\text{int}} = 0.013$
$T_{\text{min}} = 0.023$ , $T_{\text{max}} = 0.026$	$\theta_{\text{max}} = 25.1^\circ$
5021 measured reflections	$h = -8 \rightarrow 8$
	$k = -11 \rightarrow 11$
	$l = -12 \rightarrow 11$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 0.4865P]$
$R[F^2 > 2\sigma(F^2)] = 0.029$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.085$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.42 \text{ e \AA}^{-3}$
2433 reflections	$\Delta\rho_{\text{min}} = -0.52 \text{ e \AA}^{-3}$
199 parameters	Extinction correction: <i>SHELXL97</i>
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.186 (6)

H atoms of the NH groups were located in difference Fourier maps and refined freely. All remaining H atoms were placed in calculated positions and allowed to ride on their parent atoms at distances of 0.97 Å, with  $U_{\text{iso}}(\text{H})$  values equal to  $1.2U_{\text{eq}}$  of the parent atoms.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

**Table 1**

Selected geometric parameters (Å, °).

Cr2—O5	1.581 (2)	Cr3—O10	1.618 (2)
Cr2—O6	1.594 (2)	Cr3—O7	1.817 (2)
Cr2—O4	1.702 (2)	Cr1—O1	1.587 (2)
Cr2—O7	1.7195 (19)	Cr1—O3	1.601 (3)
Cr3—O8	1.5947 (19)	Cr1—O2	1.614 (2)
Cr3—O9	1.602 (2)	Cr1—O4	1.837 (2)
O5—Cr2—O6	108.74 (12)	O9—Cr3—O7	109.18 (12)
O5—Cr2—O4	111.28 (12)	O10—Cr3—O7	107.69 (11)
O6—Cr2—O4	109.73 (11)	O1—Cr1—O3	110.76 (16)
O5—Cr2—O7	108.80 (11)	O1—Cr1—O2	111.56 (14)
O6—Cr2—O7	107.38 (11)	O3—Cr1—O2	110.19 (13)
O4—Cr2—O7	110.80 (11)	O1—Cr1—O4	109.14 (11)
O8—Cr3—O9	110.10 (12)	O3—Cr1—O4	106.17 (13)
O8—Cr3—O10	110.28 (11)	O2—Cr1—O4	108.85 (10)
O9—Cr3—O10	111.71 (12)	Cr2—O7—Cr3	132.80 (12)
O8—Cr3—O7	107.76 (10)	Cr2—O4—Cr1	127.34 (12)
N1—C1—C2—N2	-13.7 (3)	N1—C5—C6—N2	-12.3 (3)
N1—C3—C4—N2	-13.9 (4)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
N1—H1···O10	0.86 (4)	1.90 (4)	2.738 (4)	164 (3)
N2—H2···O2 <sup>i</sup>	0.84 (4)	2.13 (3)	2.868 (3)	147 (3)
N2—H2···O11 <sup>ii</sup>	0.84 (4)	2.31 (4)	2.893 (4)	127 (3)
C6—H6A···O5 <sup>iii</sup>	0.97	2.48	3.339 (4)	147
C6—H6B···O8 <sup>iv</sup>	0.97	2.33	3.199 (3)	148
C4—H4B···O9 <sup>i</sup>	0.97	2.55	3.348 (3)	140
C4—H4B···O8 <sup>i</sup>	0.97	2.39	3.294 (4)	154
C4—H4A···O2 <sup>iv</sup>	0.97	2.47	3.419 (3)	168
C5—H5A···O6 <sup>v</sup>	0.97	2.42	3.135 (4)	131
C5—H5A···O5 <sup>iv</sup>	0.97	2.37	3.020 (3)	124

Symmetry codes: (i) 1 -  $x$ , - $y$ , 1 -  $z$ ; (ii) 1 +  $x$ ,  $y$ , 1 +  $z$ ; (iii) 1 -  $x$ , 1 -  $y$ , 1 -  $z$ ; (iv)  $x$ ,  $y$ , 1 +  $z$ ; (v) - $x$ , 1 -  $y$ , 1 -  $z$ .

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1645). Services for accessing these data are described at the back of the journal.

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