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Diazabicyclo[2.2.2]octane-1,4-diium dichromate

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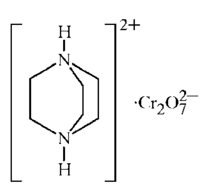
The title compound, $(C_6H_{14}N_2)[Cr_2O_7]$, consists of a diazabicyclo[2.2.2]octane-1,4-diium cation and a discrete dichromate anion, which are linked in the crystal by N—H···O hydrogen bonds. The cation is ordered and distorted, owing to the confinement and twist of the hydrogen bonds involved. Two CrO_4 tetrahedra are joined through a shared O atom to form the dichromate anion. Chiral supramolecular chains of the title compound are built up *via* N—H···O hydrogen bonds, and C—H···O interactions play subordinate roles in forming the structure.

Comment

Chromates may exist as mono-, di-, tri-, tetra- and polymeric forms (Pressprich *et al.*, 1988; Wang *et al.*, 2003; Yim & Nam, 2004; Fouada *et al.*, 1999). As no theory can currently predict the real state of these chromium compounds, many experimental attempts to find new chromates have been made since the turn of the century. We have now synthesized the title salt, (I), and its structure is compared with those of other chromates.



(I)

Fig. 1 shows the asymmetric unit of the counterbalanced ion pair of (I), which consists of a diprotonated diazabicyclo-[2.2.2]octane (DABCO) dication and a discrete dichromate anion, linked *via* an N1—H1···O2 hydrogen bond (Table 2). The dichromate anion is composed of two CrO_4 tetrahedra joined through a shared O atom. The bridging Cr—O bond lengths, Cr1—O4 and Cr2—O4, are longer than the terminal Cr—O bonds. The O—Cr—O angles range from 106.82 (10) to 111.68 (11)°. Therefore, the coordination geometries formed by the four O atoms around each Cr atom are distorted tetrahedra. The bond lengths and angles are in good agreement with those found in bipyridinium dichromates (Martín-Zarza *et al.*, 1995), bis(octyltrimethylammonium) dichromate (Fossé *et al.*, 1998) and tetramethylammonium dichromate (Fossé *et al.*, 2001). $(CrO_3)_n$ is an extreme case of a polychromate, where chains of corner-sharing CrO_4 tetrahedra extend along the whole crystal (Stephens & Cruickshank, 1970). In (I), the bridging Cr—O bond distance is obviously longer than that in $(CrO_3)_n$ (1.748 Å), and the terminal Cr—O distances are comparable with those in $(CrO_3)_n$ (1.599 Å).

Compound (I) demonstrates a hydrogen-bonding network of N—H···O and C—H···O interactions, which is similar to what is observed in diprotonated DABCO trichromate (Ding *et al.*, 2004). There are bifurcated hydrogen bonds between the cations and the anions, namely N1—H1···O2 and N1—H1···O1^{i}, and N2—H2···O7^{ii} and N2—H2···O5^{iii} (symmetry codes and geometric details are given in Table 2). On close inspection, two chiral supramolecular chains of (I) are observed, which could be described in graph-set notation (Etter, 1990) as $C_2^2(11)$. One chain is formed *via* N1—H1···O2 and N2—H2···O7^{ii} interactions and runs along the *c* axis (Fig. 3), and another is formed *via* N1—H1···O2 and N2—H2···O5^{iii} interactions and runs along the *b* axis (Fig. 2). These chains are joined by a number of C—H···O interactions, of which the shortest is C1—H1*A*···O1^{i} (Table 2). Hydrogen-bonded chains are formed in (I), rather than the hydrogen-bonded rings observed in diprotonated DABCO trichromate.

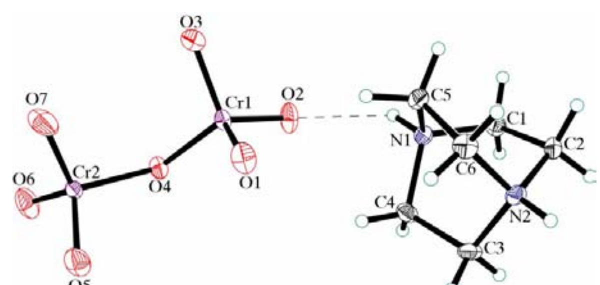


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed line indicates one of the intramolecular hydrogen bonds.

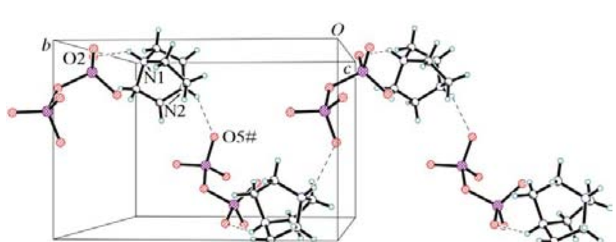


Figure 2
The chiral supramolecular $C_2^2(11)$ chain of (I), which is formed *via* N—H···O hydrogen bonds (indicated by dashed lines), viewed along the *b* axis. The atom labelled with a hash (#) is at the symmetry position $(1-x, y-\frac{1}{2}, \frac{1}{2}-z)$.

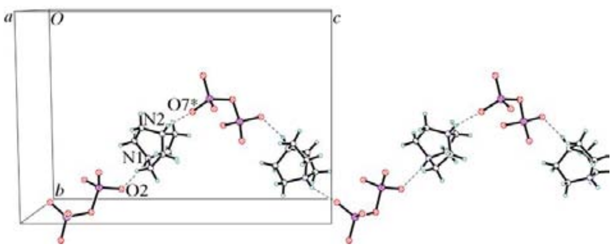


Figure 3
The chiral supramolecular $C_2^2(11)$ chain of (I), which is formed *via* N—H···O hydrogen bonds (indicated by dashed lines), viewed along the *c* axis. The atom labelled with an asterisk (*) is at the symmetry position (x, $\frac{3}{2} - y$, $z + \frac{1}{2}$).

DABCO may assume one of several conformations, namely ordered and non-distorted, ordered and distorted, disordered and non-distorted, or disordered and distorted (Nimmo & Lucas, 1976). Disordered conformations are frequently observed, such as 1:1 DABCO–biphenol (Ferguson *et al.*, 1998), 1:1 DABCO–perchloric acid (Katrusiak, 2000) and 1:2 DABCO–maleic acid (Sun & Jin, 2002). In (I), the diprotonated DABCO is ordered and distorted, owing to the confinement and twist of the above-mentioned hydrogen bonds. The situation is similar to that in diprotonated DABCO trichromate. In (I), the N—C—C—N torsion angles, with a mean value of 17.1 (3)°, indicate such a large distortion as to be comparable with the motif in an encapsulated diprotonated DABCO (Jin *et al.*, 2003).

Experimental

CrO_3 (0.2 mol) and DABCO (0.1 mol) were dissolved separately in water (1.5 and 1.2 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 the water at 298 K for a week.

Crystal data

$(C_6H_{14}N_2)[Cr_2O_7]$
M_r = 330.19
Orthorhombic, *Pbca*
a = 9.0727 (4) Å
b = 12.9327 (5) Å
c = 19.0201 (8) Å
V = 2231.71 (16) Å^3
Z = 8
D_x = 1.965 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5621 reflections
θ = 2.9–25.2°
μ = 1.97 mm^{-1}
T = 298 (2) K
Block, red
0.34 × 0.27 × 0.23 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: by integration (*SADABS*; Bruker, 2000)
T_{min} = 0.554, T_{max} = 0.660
10 994 measured reflections
2005 independent reflections
1889 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 25.2°
$h = -10 \rightarrow 10$
$k = -14 \rightarrow 15$
$l = -19 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.081
S = 1.09
2005 reflections
163 parameters
H atoms treated by a mixture of restrained and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0435P)^2 + 2.1654P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}
Extinction correction: *SHELXTL* (Bruker, 2000)
Extinction coefficient: 0.0075 (5)

Table 1
Selected geometric parameters (Å, °).

Cr1—O3	1.612 (2)	N1—C5	1.498 (3)
Cr1—O2	1.6153 (18)	N1—C4	1.502 (3)
Cr1—O1	1.6153 (18)	N2—C3	1.493 (3)
Cr1—O4	1.7847 (16)	N2—C6	1.495 (3)
Cr2—O7	1.598 (2)	N2—C2	1.501 (3)
Cr2—O6	1.602 (2)	C1—C2	1.521 (3)
Cr2—O5	1.608 (2)	C3—C4	1.524 (3)
Cr2—O4	1.7921 (17)	C5—C6	1.532 (4)
N1—C1	1.493 (3)		
O3—Cr1—O2	109.08 (11)	O7—Cr2—O5	111.05 (15)
O3—Cr1—O1	111.68 (11)	O6—Cr2—O5	109.28 (11)
O2—Cr1—O1	109.87 (10)	O7—Cr2—O4	108.46 (10)
O3—Cr1—O4	107.78 (9)	O6—Cr2—O4	106.82 (10)
O2—Cr1—O4	107.32 (9)	O5—Cr2—O4	109.97 (10)
O1—Cr1—O4	110.99 (9)	Cr1—O4—Cr2	121.36 (9)
O7—Cr2—O6	111.16 (16)		
N1—C1—C2—N2	17.0 (3)	N1—C5—C6—N2	17.8 (3)
N2—C3—C4—N1	16.6 (3)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2	0.93 (2)	2.09 (2)	2.841 (3)	137 (2)
N1—H1···O1^{i}	0.93 (2)	2.31 (3)	2.943 (3)	125 (2)
N2—H2···O7^{ii}	0.87 (3)	1.95 (3)	2.720 (3)	148 (3)
N2—H2···O5^{iii}	0.87 (3)	2.39 (3)	2.992 (3)	127 (2)
C1—H1*A*···O1^{i}	0.97	2.42	3.023 (3)	120
C1—H1*A*···O6^{iv}	0.97	2.47	3.348 (3)	151
C1—H1*B*···O6^{v}	0.97	2.55	3.299 (3)	135
C2—H2*A*···O3^{ii}	0.97	2.44	3.344 (3)	156
C3—H3*A*···O3^{vi}	0.97	2.57	3.049 (3)	111
C3—H3*A*···O6^{iii}	0.97	2.44	3.291 (3)	146
C3—H3*B*···O6^{v}	0.97	2.50	3.353 (4)	147
C4—H4*A*···O5^{i}	0.97	2.50	3.234 (3)	132
C4—H4*B*···O1	0.97	2.57	3.397 (3)	144
C5—H5*A*···O1	0.97	2.49	3.323 (3)	144
C5—H5*B*···O4^{iv}	0.97	2.56	3.443 (3)	151

Symmetry codes: (i) $x - \frac{1}{2}, y, \frac{1}{2} - z$; (ii) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (iii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (v) $\frac{1}{2} - x, 2 - y, \frac{1}{2} + z$; (vi) $\frac{1}{2} + x, y, \frac{1}{2} - z$.

The H atoms of the NH groups were located in difference Fourier maps and refined with the N—H distances restrained. All remaining H atoms were placed in calculated positions and allowed to ride on their parent atoms, with C—H = 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (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*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1676). Services for accessing these data are described at the back of the journal.

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