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Piperazinium dichromate(VI)

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Key indicators

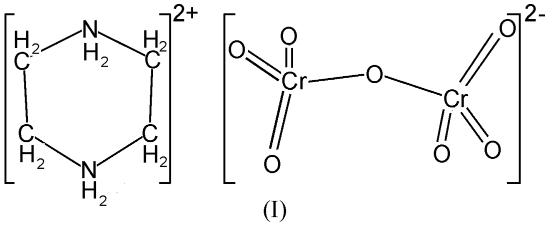
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.026
wR factor = 0.078
Data-to-parameter ratio = 21.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The structure of the title complex, $(C_4H_{12}N_2)[Cr_2O_7]$, consists of dichromate dianions which are connected to the cyclic organic piperazinium $(pipH_2)^{2+}$ dications *via* hydrogen bonding. There are two crystallographically independent piperazinium dications, both located on centres of inversion, while the anions are located in general positions.

Comment

The reported synthesis and structural characterization of complexes such as $[M(py)_4Cr_2O_7]$ (M = Cu, Zn; py = pyridine), which exhibit non-linear optical properties (Norquist *et al.*, 2001), is an important reason for the renewed interest in the chemistry of dichromate complexes associated with organic cations. Dichromates are well known for their use in organic syntheses to effect a variety of synthetic transformations (House, 1977). It has been reported that the type of the ammonium cation associated with the dichromate determines the oxidizing property of the dichromate ion and this is inversely related to the donor strength of the associated amine ligand (Santaniello *et al.*, 1983). The clue to the differing oxidizing property lies in understanding the nature of cation–anion interactions. In our work, we have been investigating the synthesis and structural characterization of materials resulting from the interaction of organic diamines with group(VI) oxo and thiometalates. All compounds hitherto reported by us exhibit weak hydrogen-bonding interactions between the organic cation and the anion. We have previously described the structures of several tetrathiomolybdates (Srinivasan *et al.*, 2004, and references therein), tetrathiotungstates (Srinivasan *et al.*, 2003*a*, and references therein), piperazinium chromate (Srinivasan *et al.*, 2003*b*) and ethylenediammonium dichromate (Srinivasan *et al.*, 2003*c*). In continuation of this work, we describe the structure of piperazinium dichromate. In separate research, this complex was shown to be a mild reagent for the oxidation of thiols to disulfides (Movassagh *et al.*, 2002).



(I)

The structure of the title compound, (I), consists of $[Cr_2O_7]^{2-}$ dianions and cyclic piperazinium dications (Fig. 1). There are two crystallographically independent cations, both located on centres of inversion, while the anions are located in general positions. As expected, the piperazinium dication

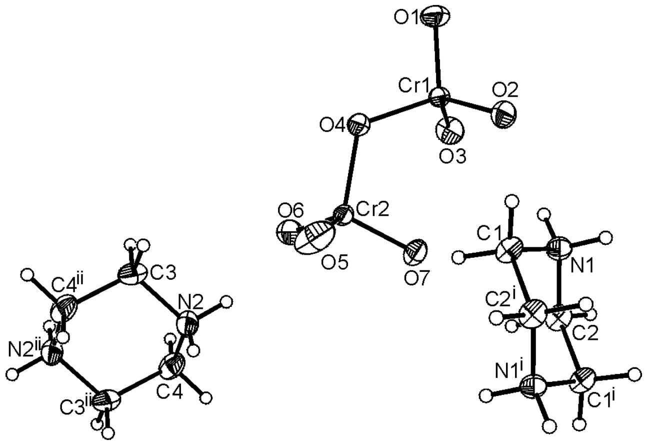


Figure 1
The crystal structure of piperazinium dichromate(VI), with labelling and displacement ellipsoids drawn at the 50% probability level [symmetry codes: (i) $2 - x, 2 - y, 1 - z$; (ii) $1 - x, 1 - y, -z$].

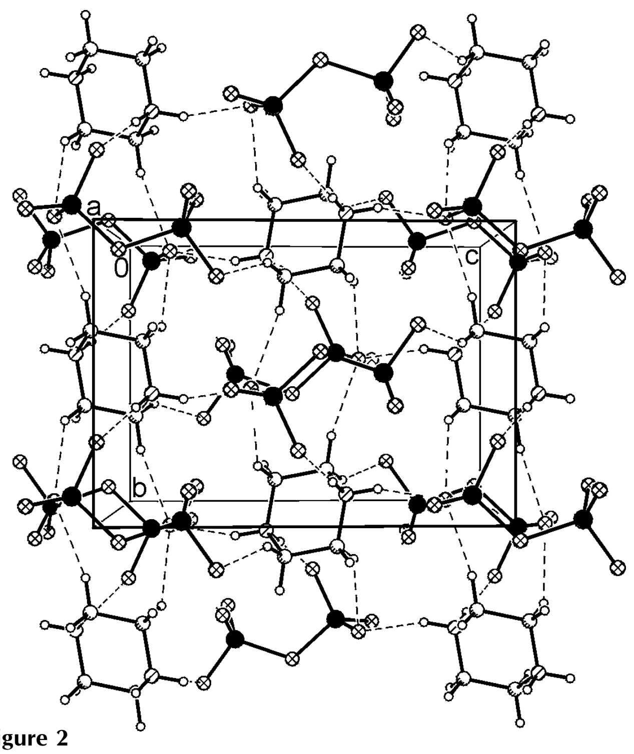


Figure 2
The crystal structure of piperazinium dichromate(VI), viewed along the *a* axis (intermolecular hydrogen bonds are shown as dashed lines).

adopts the chair conformation with bond lengths and angles (Table 1) in the range usually observed in this form (Srinivasan *et al.*, 2003*b*; Tran Qui & Palacios, 1990). The O—Cr—O bond angles range from 106.69 (7) to 111.67 (8)° (Table 1), while the terminal Cr—O bond distances in (I) vary from 1.5939 (16) to 1.6334 (14) Å, with a mean terminal Cr—O bond length of 1.6146 Å. The average bridging Cr—O bond distance is 1.7860 Å. These values are in good agreement with those reported for other dichromates (Srinivasan *et al.*, 2003*c*; Panagiotopoulos & Brown, 1972). The terminal Cr—O bond lengths in (I) cover a wider range than in the related complex $(enH_2)[Cr_2O_7]$ (enH_2 is ethylenediammonium), where the terminal Cr—O bond distances vary from 1.6075 (15) to 1.6236 (14) Å. It is also noted that the difference between the longest and the shortest terminal Cr—O bonds is of the order of 0.0395 Å, whereas in $(enH_2)[Cr_2O_7]$ the difference amounts to 0.0161 Å. Such differences can be attributed to the differing nature of the cations in the two complexes.

The cations and anions are connected *via* hydrogen bonding between the O atoms of the dianion and the H atoms bound to the nitrogen of the cyclic cation (Fig. 2). Short H$\cdots$O contacts ranging from 1.91 to 2.56 Å are observed in (I) between the O1/2/5/6/7 atoms and the H atoms of the piperazinium cation (Table 2). The shortest H$\cdots$O separation of 1.91 Å in (I) is slightly shorter than that in $(enH_2)[Cr_2O_7]$, which has a shortest contact of 1.95 Å. Atom O2 in (I) is involved in two hydrogen bonds, which explains the elongation of the Cr1—O2 distance, the longest terminal Cr—O bond in (I). Atoms O6 and O7 each have a single short hydrogen-bonding contact of 1.91 and 1.93 Å, respectively, which are accompanied by large D—H$\cdots$$A$ angles (Table 2). Hence, the observed Cr2—O6 and Cr2—O7 bond lengths of 1.6189 (16) and 1.6242 (14) Å are due to the relatively strong O6$\cdots$H and O7$\cdots$H interactions. A long H$\cdots$O distance of 2.36 Å and a small D—H$\cdots$$A$ angle of 121° indicate a very weak interaction and consequently the Cr2—O5 bond is the shortest [1.5939 (16) Å]. The intermediate Cr1—O1 bond length of 1.6068 (14) Å can be similarly explained based on the strength of the hydrogen-bonding interaction.

Experimental

$(NH_4)_2[Cr_2O_7]$ (1.512 g) was dissolved in distilled water (10 ml) containing 0.3 ml of concentrated H_2SO_4 and this solution was slowly added to a solution of piperazine hexahydrate (1.2 g) dissolved in water (4 ml), resulting in the formation of yellow–orange crystalline blocks of the title complex. The crystals were filtered off, washed with ice-cold water (1 ml) and dried in air (yield 85%). The crystals are quite stable in air. Analysis calculated for $C_4H_{12}Cr_2N_2O_7$: C 15.79, H 3.98, N 9.21%; found: C 15.17, H 4.11, N 9.39%. ^{1}H NMR (D_2O, 300 MHz): 3.44 p.p.m. (*s*, 8H).

Crystal data

$(C_4H_{12}N_2)[Cr_2O_7]$
$M_r = 304.16$
Monoclinic, $P2_1/c$
$a = 11.654$ (2) Å
$b = 7.8702$ (6) Å
$c = 10.855$ (2) Å
$\beta = 93.42$ (1)°
$V = 993.8$ (3) Å^3
$Z = 4$

$D_x = 2.033$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 86 reflections
$\theta = 26$–38°
$\mu = 2.21$ mm^{-1}
$T = 293$ (2) K
Block, orange
$0.13 \times 0.11 \times 0.07$ mm

Data collection

Stoe AED-II four-circle diffractometer
ω–θ scans
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1998)
$T_{min} = 0.755$, $T_{max} = 0.860$
3793 measured reflections
2901 independent reflections
2459 reflections with $I > 2\sigma(I)$

$R_{int} = 0.033$
$\theta_{max} = 30.0$°
$h = -16 \rightarrow 16$
$k = -2 \rightarrow 11$
$l = -15 \rightarrow 0$
4 standard reflections
frequency: 120 min
intensity decay: none

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.078$
$S = 1.07$
2901 reflections
137 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.044P)^2 + 0.3618P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.51$ e Å^{-3}
$\Delta\rho_{\min} = -0.62$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0126 (13)

Table 1
Selected geometric parameters (Å, °).

Cr1—O1	1.6068 (14)	N1—C2	1.487 (2)
Cr1—O3	1.6101 (14)	N1—C1	1.498 (2)
Cr1—O2	1.6334 (14)	C1—C2^{i}	1.512 (2)
Cr1—O4	1.7890 (13)	C2—C1^{i}	1.512 (2)
Cr2—O5	1.5939 (16)	N2—C3	1.484 (3)
Cr2—O6	1.6189 (16)	N2—C4	1.490 (3)
Cr2—O7	1.6242 (14)	C3—C4^{ii}	1.504 (3)
Cr2—O4	1.7830 (13)	C4—C3^{ii}	1.504 (3)
O1—Cr1—O3	110.06 (8)	O6—Cr2—O4	108.91 (7)
O1—Cr1—O2	108.25 (8)	O7—Cr2—O4	107.67 (7)
O3—Cr1—O2	111.67 (8)	Cr2—O4—Cr1	117.79 (7)
O1—Cr1—O4	106.69 (7)	C2—N1—C1	111.69 (13)
O3—Cr1—O4	109.60 (7)	N1—C1—C2^{i}	110.06 (14)
O2—Cr1—O4	110.44 (7)	N1—C2—C1^{i}	110.47 (14)
O5—Cr2—O6	111.42 (11)	C3—N2—C4	111.69 (15)
O5—Cr2—O7	110.45 (8)	N2—C3—C4^{ii}	110.97 (15)
O6—Cr2—O7	109.88 (8)	N2—C4—C3^{ii}	109.77 (15)
O5—Cr2—O4	108.41 (9)		

Symmetry codes: (i) $2 - x, 2 - y, 1 - z$; (ii) $1 - x, 1 - y, -z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1N1$\cdots$O2	0.90	2.08	2.878 (2)	148
N1—H1N1$\cdots$O5^{iii}	0.90	2.36	2.925 (2)	121
N1—H2N1$\cdots$O2^{iv}	0.90	2.04	2.893 (2)	159
N1—H2N1$\cdots$O1^{iv}	0.90	2.56	3.227 (2)	132
N2—H1N2$\cdots$O7^{v}	0.90	1.93	2.828 (2)	174
N2—H2N2$\cdots$O6	0.90	1.91	2.779 (2)	162

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

The C—H and N—H H atoms were positioned with idealized geometry (C—H = 0.97 Å and N—H = 0.90 Å) and refined with fixed isotropic displacement parameters according to the riding model [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(methylene C,N)].

Data collection: *DIF*4 (Stoe & Cie, 1992); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1992); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *CIFTAB* in *SHELXTL*.

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